RYDBERG STATES OF DIATOMIC AND POLYATOMIC MOLECULES USING MODEL POTENTIALS

Thesis by

Timothy Charles Betts

In Partial Fulfillment of the Requirements

For the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1972

(Submitted December 16, 1971)

Acknowledgments

I wish to express my appreciation to Dr. Vincent McKoy for suggesting the project described in this thesis and for discussion and advice given throughout the course of my studies.

I would also like to thank Dr. Nicholas W. Winter for advice and assistance with various stages of programming encountered in this work.

Finally, I would like to thank my wife, Jeanette, for the encouragement and support she has given me in the preparation of this thesis.

Abstract

A simple model potential is used to calculate Rydberg series for the molecules: nitrogen, oxygen, nitric oxide, carbon monoxide, carbon dioxide, nitrogen dioxide, nitrous oxide, acetylene, formaldehyde, formic acid, diazomethane, ketene, ethylene, allene, acetaldehyde, propyne, acrolein, dimethyl ether, 1, 3-butadiene, 2-butene, and benzene. The model potential for a molecule is taken as the sum of atomic potentials, which are calibrated to atomic data and contain no further parameters. Our results agree with experimentally measured values to within 5-10% in all cases. The results of these calculations are applied to many unresolved problems connected with the above molecules. Some of the more notable of these problems are the reassignment of states in carbon monoxide, the first ionization potential of nitrogen dioxide, the interpretation of the V state in ethylene, and the mystery bands in substituted ethylenes, the identification of the R and R′ series in benzene and the determination of the orbital scheme in benzene from electron impact data.

TABLE OF CONTENTS

1. RYDBERG SERIES

Any group of atomic or molecular states of the same spin and orbital symmetry whose term values ν follow the simple formula:

$$(1)\quad \nu = \text{I.P.} - R/(n - \delta)^2 \qquad n = 1, 2, 3\cdots$$

where I.P., R, and δ are constants, are said to belong to a Rydberg series, and the states are called Rydberg states. In the above formula I.P. is called the ionization limit of the series, R is the Rydberg constant $\sim$ 109,677.581 cm^{-1} (13.595 eV) and δ is the quantum defect. In most cases the quantum defect δ depends somewhat on the value of n, but this dependence is very slight and is usually ignored.

The above definition is a purely experimental definition and would have been discarded long ago had it not proven itself useful. The fact that there are Rydberg series, and indeed Rydberg series are observed in practically every atom and molecule, suggests that there is some common, underlying physics behind the simple Rydberg formula. This is indeed the case. It has been both inferred experimentally and demonstrated by calculations that Rydberg states correspond to states with an electronic configuration such that an electron in an orbital, the Rydberg orbital, occupies mainly a regional space exterior to the region occupied by the other electrons. These other electrons and the associated nuclei constitute the "core" about which the Rydberg electron

travels in much the same fashion as it would travel about an effective potential field derived from these electrons and nuclei. The different members of the Rydberg series correspond to different Rydberg orbitals of the same symmetry which occupy positions more and more removed from the core potential.

The details of how this comes about for atomic sodium have been given by Slater.[1] We shall give a treatment similar to Slater's here.

First we note that for sodium the Rydberg electron moves in the potential field created by the nucleus and the inner filled shells of electrons. The charge density of these filled shells is spherically symmetrical; furthermore the motion of the electrons within these shells is practically independent of the behavior of the outer electron. This means that we may replace the effect of the nucleus and the inner filled shells of electrons with a single, spherically symmetric potential field which is the same for all of the possible Rydberg states of sodium.

The analytical form of this field for sodium, $Zp(r)$, has been given by Slater[2] and is reproduced in Figure 1a. We note that for r greater than about 1.5 a.u. the field becomes hydrogenic. But the energies of sodium are not the same as those for hydrogen. This means that the outer part of the wavefunctions for the Rydberg orbitals correspond to the general solutions of the hydrogen radial wave equation with energies equal to the energies of the sodium atom. These solutions, which go to zero as r approaches infinity, are valid down to $r_0 = 1.5$ a.u. For values

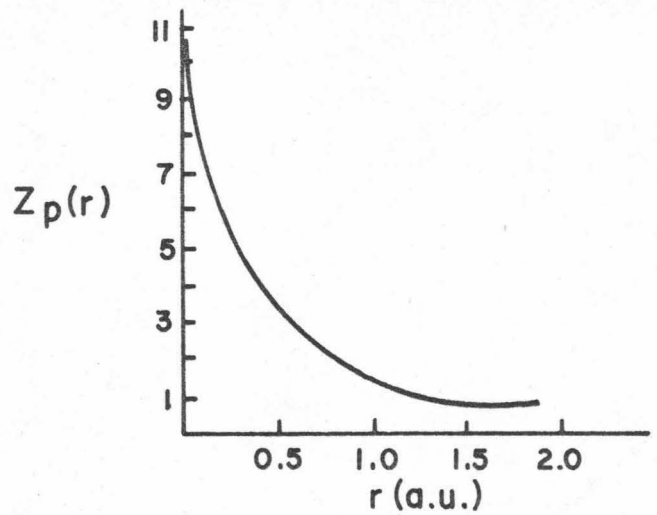


Figure 1a. $Z_p(r)$ as a Function of r

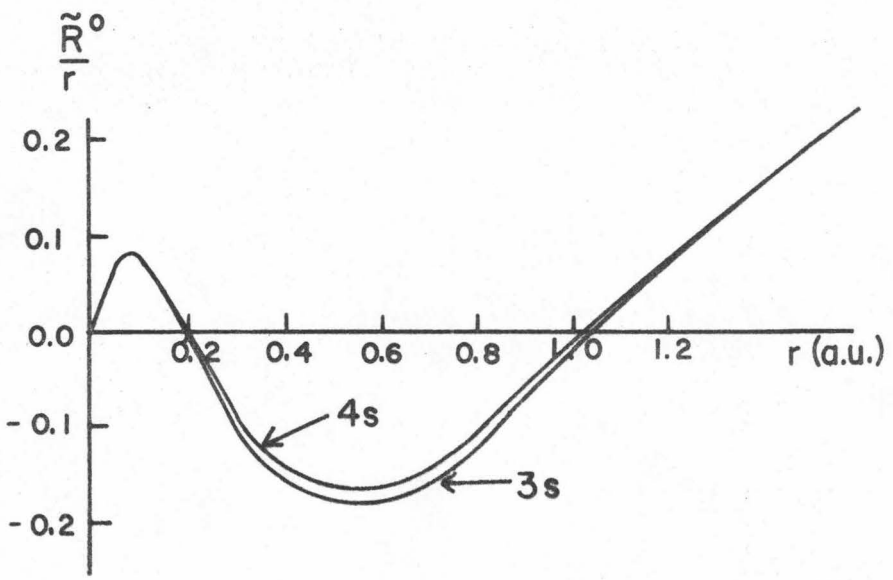


Figure 1b. Solutions for the Slater Potential

of r smaller than this, the wavefunctions of the Rydberg orbitals are solutions of the Schrödinger equation with the sodium potential given by Slater. These solutions, which behave properly at the origin, are the be joined on to the general hydrogenic solutions at r = 1.5 a.u.

To proceed further we must investigate the nature of the general solutions of the hydrogen radial wave equation. Proofs for the statements we make here will be postponed until the section on Atomic Calibration.

Figure 2 I-VII shows a series of graphs of the general hydrogen solution for $\ell = 1$ in the vicinity of the origin. This function is a function of both r and energy. Each graph corresponds to a different energy. As the energy increases from $E \ll -13.6$ eV to $E \simeq -1.5$ eV the function takes on the form shown in graphs 1, 2, 3, $\cdots$ etc. The important feature to notice is that at the energies corresponding to the hydrogen atom solutions 5, 10, etc., a node is formed at the origin and once formed this node continues to move outward from the origin. In general, the solution of the hydrogen radial wave equation with $-13.6/(n+1)^2 \leq E < -13.6/(n+2)^2$ eV has exactly n nodes. It is possible to renormalize the functions from Figure 2 III-VII so that they appear as in Figure 3 I-VIII. In these graphs the designation of the solution is the same as in Figure 2, but the ordinates are not necessarily to the same scale either with those of Figure 2 or with one another.

We can see that the solution has the general appearance of a periodic wave as a function of energy for these small values of

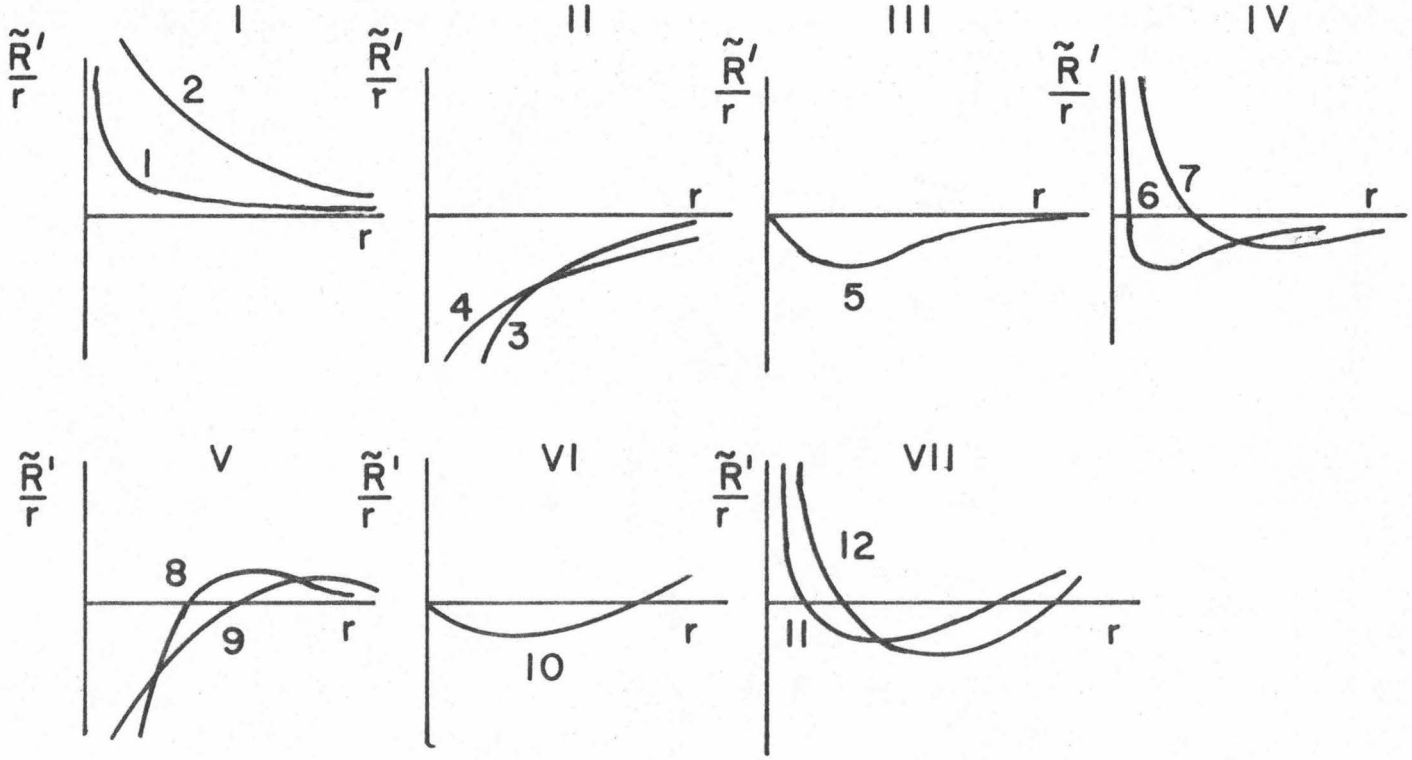


Figure 2. Solutions of the Hydogen Radial Wave Equation

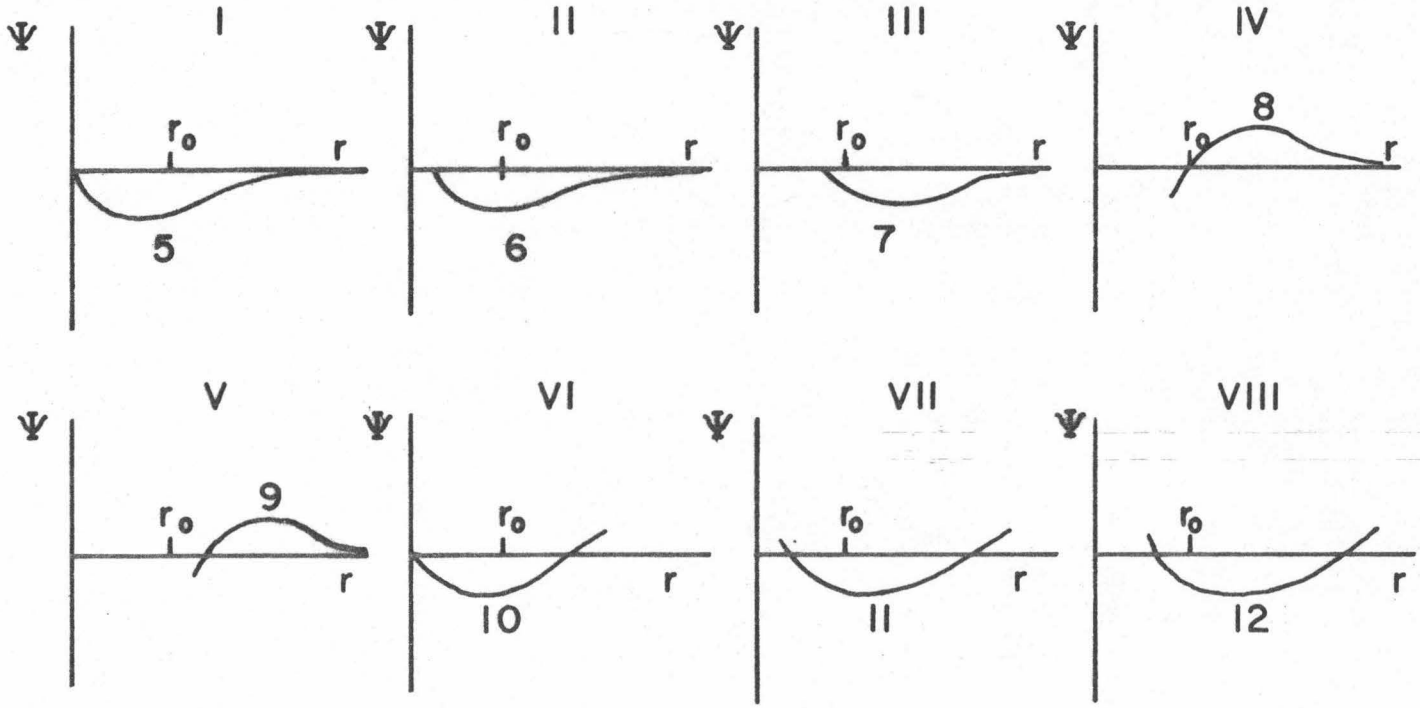


Figure 3. Renormalized Hydrogen Radial Wave Equation Solutions.

r. The period is equal to 1 in terms of the variable n, where $n = \sqrt{R/E}$ and E is measured in Rydbergs. This being the case, we can classify the solutions of the hydrogen radial wave equation with respect to the phase δ that this periodic wave has with some point r_0. Setting the phase of the hydrogen atom solutions equal to zero, the energies of the solutions with phase δ will have the values:

$$(2) \quad E_n = -R/(n - \delta)^2 \qquad n = 1, 2, 3 \cdots$$

Finally, we note that since the solutions with phase δ are all represented by essentially the same periodic wave in the region of small r, their boundary conditions are all necessarily the same too. We will find this property most useful later on.

Next, we turn to the investigation of the solution of the Schrödinger equation for the sodium atom potential. It is found that for small r's the solutions of this equation are nearly independent of energy for a reasonable range of energy, i.e. -5 eV < E < 0 eV. This can be seen in Figure 1b, taken from Slater,[3] where the 3s and 4s functions calculated for Slater's sodium potential have been plotted for small values of r. The functions have been renormalized so as to agree as closely as possible over this range. The reason for this approximate independence of energy is that in this range of r the effective potential term of the Schrödinger equation $2\mu e^2 Zp(r)/\hbar^2 r - \ell(\ell + 1)/r^2$ is very large numerically compared with the energy eigenvalue term $2\mu E_n/\hbar^2$. Thus small variations in E_n make very small relative changes in

the classical kinetic energy, and hence in the wavefunction. In more physical terms, when the electron penetrates into the interior of the atom, where Zp(r) is larger than unity, it speeds up so much on account of the nuclear attraction that its motion is almost independent of the very small amount of kinetic energy which it had when it entered the atom.

Knowing the properties of the general hydrogen solution and the solutions of the Schrödinger equation for the sodium potential Zp(r), we must now join these functions together at our boundary r_0 = 1.5 a.u. From the above, we know that all of the solutions for the sodium potential have practically identical boundary conditions at r_0 = 1.5 a.u. since they are nearly energy independent for this range of r. Using these boundary conditions we search for the energy which corresponds to the general hydrogen solution with the same set of boundary conditions at $r = r_0$. Once this energy is found, we can determine the phase of this solution, and immediately we know of a discrete infinity of solutions with the same boundary conditions, i.e., those solutions which have the same phase as our original solution. These other general hydrogen solutions must join onto the other sodium potential solutions since the boundary conditions are the same at $r = r_0$, and we have constructed all of the wavefunctions for the Rydberg orbitals. The energies of these Rydberg orbitals will then be:

$$(3) \quad E_n = -R/(n - \delta)^2 \qquad n = 1, 2, 3 \cdots$$

We see from the arguments above that the dependence of δ upon n is a function of how nearly alike the boundary conditions are for the general hydrogen solution with the same phase; and how energy independent the solutions of the sodium potential are. In practice these approximations hold to a very high degree so that δ is independent of n to within a few percent.

Formula 3 can be made to agree with formula 1 given at the beginning of this section by noting that as n becomes large E_n in formula 3 approaches zero and the Rydberg orbital moves farther from the core. In the limit the sodium atom is ionized; hence we see that the purpose of the constant I. P. is simply to shift the energy scale to give this experimentally measured ionization potential its correct value. Thus all of the terms of equation 1 have now been accounted for.

The above arguments have given us the general form of the Rydberg formula, but they do nothing to tell us about how δ depends on ℓ. For sodium δ is about 1.35 for s levels, it is 0.86 for p levels, but very small for d and f levels. It is found that the magnitude of the quantum defect δ depends on the amount of penetration of the Rydberg orbital into the interior of the atom. If we were to plot d and f Rydberg orbitals for the region where Zp(r) is not unity as we did for the s orbitals in Figure 1b, we would find that they were very small in this region. Hence their boundary condition is that they are practically zero with zero slope at $r_0 = 1.5$ a.u. These are the same boundary conditions that the d and f functions of the hydrogen atom obey. Hence these

energy levels are practically the same as for hydrogen (i.e., quantum defect $\delta \approx 0$). On the other hand, the s and p Rydberg orbitals must penetrate significantly into the core where $Z_p(r)$ is not unity. The reason for this is that a Rydberg orbital with, say, s symmetry must be orthogonal to all other orbitals with the same symmetry. This includes the core orbitals. In order to be orthogonal to the core orbitals, the Rydberg orbital must have significant density within the core in order for this cancellation to be possible. Thus, as a simple rule we can say that those ℓ values for which there are no occupied states in the atom will have nonpenetrating Rydberg orbitals, and their energies will be almost hydrogenic. As we go from these ℓ values to the lower ones for which there are occupied states, the Rydberg orbitals become penetrating and the quantum defect δ increases very rapidly. The same argument for penetrating and nonpenetrating orbitals holds for diatomic and polyatomic molecules as well as for atoms. Occupied core orbitals of the same symmetry as a Rydberg orbital are sometimes called precursors of the Rydberg orbital.

While we are still considering Rydberg states of atoms we should consider the case of nonclosed shell cores. Consider the Rydberg states of beryllium with the electronic configuration $(1s)^2(2s)(np)$. There are two Rydberg series represented by this electronic configuration corresponding to the symmetries ^3P and ^1P. The quantum defects δ for these series will be different because of the different exchange energy contributions to the singlet and triplet states. The question arises, if we are to interpret the

quantum defect δ as a phase shift as we did for the closed shell sodium core, which δ do we use, the singlet or the triplet? The answer to this question has been given by Mulliken;[4] he says, "The best practical (though approximate) assumption appears to be to use δ values corresponding to averages of observed singlet and triplet energies as suitable measures of the phase shifts." In this way the effects of the exchange contributions to the singlet and triplet states roughly cancel one another out. The same sort of averaging process should be carried out when the Rydberg states of the nonclosed shell atom are doublet and quartet, triplet and quintet, etc.

We now turn to Rydberg states of diatomic and polyatomic molecules. In the same way as we joined atomic core solutions on to the solution of the hydrogen radial wave equation to produce Rydberg orbitals in the case of the sodium atom, we want to join molecular core solutions on to the solution of the hydrogen radial wave equation to produce Rydberg orbitals for molecules. The difference between these two cases is that the molecular core no longer has the spherical symmetry that the sodium core and the general hydrogen solutions have. However, for large enough distances from the core, the core potential approaches a $-e^2/r$ hydrogenic potential, and we can expect the solutions for the core to join on smoothly to the general hydrogen solution. The major differences in the atomic and molecular cases arise as a consequence of the departure of the core from spherical symmetry farther in. For atoms we can always determine the quantum defect δ

unambiguously by counting up the number of radial nodes, noting the energy, and using the relation between the energy and number of nodes, as was given above. For molecular problems there are strong distortions of the core solutions corresponding to a mixing of spherically symmetric solutions of different n and ℓ in order to produce the proper core symmetry. This mixing destroys nodes and makes it impossible to determine quantum defects δ unambiguously, at least for penetrating orbitals. For non-penetrating orbitals this mixing usually does not interfere with the assignment of δ. When we cannot assign the quantum defects δ correctly, it is frequently wiser to classify observed Rydberg states according to their effective quantum number n*,

$$n^* = n - \delta. \tag{4}$$

This quantity has the advantage of being experimentally available. Despite this advantage we shall always classify states according to their quantum defects δ.

One way of getting around the difficulty in determining δ, for diatomic molecules at least, would seem to be to assign the quantum defects of the molecular orbitals on the basis of their United Atom limits. This has been done for some molecules. However, it has disadvantages. For instance, in nitrogen the first $p\sigma_u$ Rydberg orbital has one more precursor in the core than the first $p\pi_u$ Rydberg orbital does. This means that the two states with practically identical forms and energies must be assigned the quantum defects 1.71 and .73 respectively, which surely does not

display the close similarity which exists between these orbitals. Another more serious difficulty arises when a Rydberg state lies somewhere between its United Atom and Separated Atom limits. At these internuclear distances considerable mixing of different basis functions occurs and an orbital which becomes an $nd\pi$ orbital in the United Atom limit may look like an $np\pi$ orbital in this region. In general, the Rydberg orbitals are fairly close to their United Atom limits, but the above circumstance does arise and must be accounted for. In the following we have in general ignored the existence of precursor orbitals and have assigned our Rydberg states according to the symmetry which they display when they are plotted. In cases where this symmetry was not obvious, states were assigned to the symmetry of the Rydberg series they were a part of, according to the Rydberg formula. Rydberg states which had similar forms and energies were assigned similar quantum numbers and quantum defects regardless of the existence of precursors. Thus in effect we classify our states according to their n^* values, although our notation is in terms of δ.

In closing our discussion of Rydberg states we would like to consider nonclosed shell cores in molecular Rydberg states. Where as for atomic nonclosed shell cores we could get different Rydberg states with different spin symmetry, for diatomic and polyatomic molecules we can get Rydberg states with both different spin and different orbital symmetries. Consider the nitric oxide molecule. It can have Rydberg states with the electronic configuration:

$$(1\sigma)^2 (2\sigma)^2 (3\sigma)^2 (4\sigma)^2 (5\sigma)^2 (1\pi)^3 (2\pi) (ns\sigma)$$

corresponding to both doublet and quartet Σ^+, Σ^- and Π Rydberg series. So far only the $^2\Sigma^+$ series has been observed experimentally. As in the case with atomic nonclosed shell cores we consider the average of the quantum defects for these different Rydberg series to be comparable to the quantum defect for closed shell core molecules. When we discuss our method of calculation further, it will be seen that this average is the quantity which we calculate directly. Thus in comparing our results with experiment, we should average the experimental results over Rydberg states with the same electronic configuration.

References

1. J. C. Slater, Quantum Theory of Atomic Structure, Vol. I, McGraw Hill, New York, 1960, Section 9-8.
2. J. C. Slater, ibid., Fig. 9-5, pg. 228.
3. J. C. Slater, ibid., Fig. 9-6, pg. 231.
4. R. S. Mulliken, J. Amer. Chem. Soc. 86, 3183 (1964).

2. PSEUDOPOTENTIALS AND MODEL POTENTIALS

The pseudopotential method in its present form was introduced when solid state physicists[1] realized that in an atom, molecule or solid there is almost complete cancellation between the large negative potential energy V felt by a valence electron when inside the core of an atom, and its large positive kinetic energy, which is inherent in the oscillations of its wavefunction ψ_v there.

Mathematically this cancellation can be demonstrated by showing that the wave equation for the valence electron:

$$(1) \qquad H\psi_v = (T + V)\psi_v = E_v\psi_v$$

can be transformed into a new equation:

$$(2) \quad (H + V_p)\phi_v = (T + V + V_p)\phi_v = E_v\phi_v$$

where V_p is a nonlocal repulsive pseudopotential which cancels off most of V, leaving a weak effective potential $(V + V_p)$. In equation (2) ϕ_v is a pseudo-wavefunction which is equal to ψ_v outside the core, but inside the core has the oscillations of ψ_v removed.

There are several ways to present pseudopotentials. One way would be the historical approach[2] showing how the pseudopotential idea was developed. Another would be to show how useful they can be in solving many varied and interesting problems.[3] For our purposes we prefer to work backwards. We will first prove the most general pseudopotential theorem (which is really very

simple), then we will use this as a starting point to pick out interesting special cases and to justify our procedure. This method has the advantage of allowing us to concentrate very sharply upon the features of pseudopotentials which we will need for Rydberg states, while keeping in the background other features which we do not need.

We start[4] by calculating the eigenvalues and eigenfunctions of $H + V_p$, where V_p is defined by:

$$V_p\phi = \sum_c \langle F_c | \phi \rangle \psi_c \tag{3}$$

The F_c are completely arbitrary functions. The eigenfunctions and eigenvalues of H are denoted by E_n and ψ_n, where n = c or v according to whether we are considering core or valence states. Physically speaking, we mean by core states the inner shell electrons of an atom or molecule and by ϕ_v the Rydberg orbitals. The mathematics of the problem, however, only supposes that the eigenvalues and eigenvectors are divided into two distinct classes and does not concern itself with any differences which may exist between these classes. The eigenvalues and eigenvectors of $H + V_p$ we denote by $\tilde{E}_n$ and ϕ_n, again with n = c or v as above, i.e.:

$$(H + V_p)\phi_n = \tilde{E}_n\phi_n \qquad n = c \text{ or } v \tag{4}$$

Consider the core states and expand ϕ_c in terms of the complete orthonormal set of functions ψ_n. Then:

$$(5) \qquad \phi_c = \sum_{c'} \alpha_{c'} \psi_{c'} + \sum_{v} \alpha_v \psi_v$$

Substituting equation (5) into equation (4), and using (3), we get:

$$(6) \sum_{c'} \sum_{c''} [(E_{c'} - \tilde{E}_c)\delta_{c'c''} + \langle F_{c'} | \psi_{c''} \rangle]\alpha_{c''}\psi_{c'}$$

$$+ \sum_{c'} \sum_{v} \alpha_v \langle F_{c'} | \psi_v \rangle \psi_{c'} + \sum_{v} (E_v - \tilde{E}_c)\alpha_v \psi_v = 0$$

In the above equation the coefficient of every ψ_n must vanish identically. Looking at the coefficients of the ψ_v's we see that unless there is some accidental degeneracy between $\tilde{E}_c$ and some E_v, all of the α_v's = 0, and ϕ_c is a linear combination of the ψ_c's. Furthermore, since the last two terms of equation (6) must vanish, the energy $\tilde{E}_c$ will be given by the solution of the secular equation:

$$(7) \quad \det \left| (E_{c'} - \tilde{E}_c)\delta_{c'c''} + \langle F_{c'} | \psi_{c''} \rangle \right| = 0$$

We shall return to this equation later. For the present we are more interested in the orbitals ϕ_v which correspond to our Rydberg orbitals.

We calculate the valence states ϕ_v by expanding them in terms of the ψ_n's also:

$$(8) \qquad \phi_v = \sum_{c} \beta_c \psi_c + \sum_{v'} \beta_{v'} \psi_{v'}$$

Substituting equation (8) in equation (4), and using (3), we get:

$$(9)\quad \sum_c \sum_{c'} [(E_c - \tilde{E}_v)\delta_{cc'} + \langle F_c|\psi_{c'}\rangle]\beta_{c'}\psi_c + \sum_{v'} \sum_c \langle F_c|\psi_{v'}\rangle\beta_{v'}\psi_c + \sum_{v'} (E_{v'} - \tilde{E}_v)\beta_{v'}\psi_{v'} = 0$$

This equation can be rearranged to the form:

$$(10)\quad \sum_c \sum_{c'} [(E_c - \tilde{E}_v)\delta_{cc'} + \langle F_c|\psi_{c'}\rangle]\beta_{c'}\psi_c + \sum_c \langle F_c|\psi_v\rangle\beta_v\psi_c + (E_v - \tilde{E}_v)\beta_v\psi_v \sum_{v'\neq v} (E_{v'} - \tilde{E}_v)\beta_{v'}\psi_{v'} + \sum_{v'\neq v} \sum_c \langle F_c|\psi_{v'}\rangle\beta_{v'}\psi_c = 0$$

Again in this equation the coefficient of every ψ_n must vanish identically. Looking at the coefficient of ψ_v we see that $\tilde{E}_v = E_v$. From the coefficient of $\psi_{v'}$ we have $\beta_{v'} = 0$ unless there is some degeneracy. Thus ϕ_v has the form:

$$(11)\qquad \phi_v = \psi_v + \sum_c \beta_c\psi_c$$

where the β_c's can be determined from the nonvanishing terms of equation (10), i.e.:

$$(12)\quad \sum_{c'} [(E_c - E_v)\delta_{cc'} + \langle F_c|\psi_{c'}\rangle]\beta_{c'} = -\langle F_c|\psi_v\rangle$$

This equation must have a unique solution for the unknown coefficients $\beta_{c'}$ unless:

$$(13)\quad \det\left|(E_c - E_v)\delta_{cc'} + \langle F_c|\psi_{c'}\rangle\right| = 0$$

Comparing this criterion with equation (7), we can say that there is a unique solution for the coefficients $\beta_{c'}$ unless there is some accidental degeneracy between E_v and $\tilde{E}_c$. Throughout this proof, if some degeneracy does occur, it results in a degree of arbitrariness in the wavefunctions which may, however, still be chosen in the form described above.

This completes the proof of the general pseudopotential theorem. In essence it states that the wave equation

$$(14)\qquad H\psi_v = (T + V)\psi_v = E_v\psi_v$$

can be transformed into a new wave equation:

$$(15)\quad (H + V_p)\phi_v = (T + V + V_p)\phi_v = E_v\phi_v$$

Provided only that V_p belongs to the very general class of operators having the property:

$$(16)\qquad V_p\phi = \sum_c \langle F_c|\phi\rangle\psi_c$$

where the F_c are arbitrary functions. The general form of V_p is that of a projection operator which projects any function ϕ onto the space spanned by the functions ψ_c. An interesting special case is when $F_c = (E_v - E_c)\psi_c$. Then the pseudopotential becomes:

$$(17)\quad V_p^{P.K.}\phi = \sum_c (E_v - E_c)\langle\psi_c|\phi\rangle\psi_c$$

This is the Phillips-Kleinman pseudopotential and is interesting because its discovery led to all of the recent work on pseudopotentials.

If the above were all that we could do with pseudopotentials, there would not be nearly so much time and effort spent on them as there is. For in truth, the pseudopotential wave equation (15) can be just as difficult to solve, if not more so, than the original wave equation (14). To make any progress, we must inject some physics into this purely mathematical formalism. This will lead us ultimately to the subject of model potentials.

Our point of attack will be with the effective potential $V + V_p$. This potential depends on V_p, which in turn depends on the choice of functions F_c. We can, if we want, vary the F_c and solve the resulting pseudo-wave equations for the resulting pseudo-wavefunctions. From the definition of V_p it is clear that changes in V_p bring about changes in the effective potential $V + V_p$ primarily in the region of the core. Hopefully, then, we can find a simple effective potential which has a pseudo-wavefunction with a correspondingly simple core part. We will then use this simple effective potential for problems involving its corresponding core.

Unfortunately, for smooth effective potentials the pseudo-wavefunctions turn out to have many oscillations; and for simple, smooth pseudo-wavefunctions the corresponding effective potentials are oscillatory. Abarenkov and Heine[5] attribute this behavior to the fact that when using pseudopotentials we must work with the finite subspace of core eigenfunctions, rather than a complete set

of functions. Thus these difficulties are inherent in the method and cannot be gotten around within the pseudopotential formalism.

If we are willing to go outside of this formalism we can, however, make some progress. Our primary interest is in a simple, smooth pseudo-wavefunction. We then take the effective potential corresponding to this choice of pseudo-wavefunction, and approximate it with a simple smooth model potential. The model potential cannot represent all of the oscillations present in the original effective potential, but we do not care. What we desire is that the solutions of our model potential behave similarly to the solutions of the effective potential and provide a reasonable approximation to the pseudo-wavefunction. It is important to realize that it is not necessary to work within the pseudopotential formalism to define model potentials. One can develop the model potential in an exact and rigorous manner from an independent point of view. The only absolute requirement on a pseudo or model potential is that it gives the same energy eigenstates as the real potential.

What are, then, acceptable model potentials for atoms? Abarenkov and Heine tried several model potentials for atoms, judging their effectiveness by how good agreement they could get between a given calculated and experimental energy. Based on this study they suggested a model potential of the form:

$$(18) \qquad V_m^{A.H.}(\underset{\sim}{r}) = \sum_{\ell} V_{\ell}^{A.H.}(r)\hat{P}_{\ell}$$

where:

$$\hat{P}_\ell \phi = \sum_{m=-\ell}^{\ell} \langle Y_{\ell m}(\theta, \phi) | \phi \rangle \, Y_{\ell m}(\theta, \phi)$$

and

$$V_\ell^{A.H.}(r) = \begin{cases} -A_\ell & r \leq r_0 \\ -\delta z / r & r \geq r_0 \end{cases}$$

In the above, $Y_{\ell m}(\theta, \phi)$ is a spherical harmonic function, A_ℓ and r_0 are constants, and δz is the effective charge on the atomic ion. The model potential is written as a function of the orbital quantum number ℓ because some of the valence orbitals will be penetrating while others will be nonpenetrating, depending on their ℓ values. It was felt on a priori grounds that the model potential V_m must be very different in these different circumstances. The results of our calculations and calculations similar to ours[6] have shown that for Rydberg states at least, the effect of penetrating and nonpenetrating orbitals is more or less taken into account automatically, and that we may replace the Abarenkov-Heine model potential by simply its first term. Thus for atoms an acceptable model potential for Rydberg states is:

$$(19) \qquad V_m(\underset{\sim}{r}) = \begin{cases} A & r \leq r_0 \\ -\delta z / r & r \geq r_0 \end{cases}$$

The above potential has three adjustable parameters, A, r_0 and δz. r_0 is more or less the boundary of the core region. If we expect to get reasonable results, we see from our previous

discussion of Rydberg states, that r_0 must be of the order of 2.0 a.u. The parameter A must be determined by calculation and will be different for different atoms, δz for an atomic problem is simply equal to unity. We will return to this potential in greater detail in the section on Atomic Calibration, right now we want to go on to model potentials for molecules.

For the last few paragraphs our discussion has been limited to atoms. The problem we want to solve is that for molecules. We ask the question, what is an acceptable pseudo or model potential for a molecule? The question about pseudopotentials for molecules is still to be answered. It will probably be the subject of chemical research for many years to come. For model potentials, however, we can state something definite. Our work, and the work of Hazi and Rice[6] shows that an acceptable model potential for molecular Rydberg states is:

$$(20) \qquad V_m^{\text{Molecule}} = \sum_{\text{atoms}} V_m^{\text{atom}}$$

That is, the model potential for a molecule can be taken as the sum of the model potentials of its constituent atoms. This is a particularly simple and convenient result. It suggests that we may determine the atomic model potentials independently from some atomic property, and then simply insert these atomic potentials into our molecular problem. In this way there are no adjustable parameters in the molecular problem, all of the parameters having been fixed by the atomic calculations. This avoids a proliferation of adjustable parameters in the molecular calculation.

The results to be presented here show that this is a highly successful approach. However, there is one minor difficulty. This is due to the parameter δz, the effective charge on the atomic ion. For an atomic calculation $\delta z = 1$, as was stated above. In calculating a homonuclear diatomic molecule we know by symmetry that we may set $\delta z = \frac{1}{2}$ in each one of the atoms. But what is δz in a heteronuclear diatomic? The results of our calculations show that we may take $\delta z = \frac{1}{2}$ here also. But the problem persists for larger molecules of low symmetry. The charge distribution for these molecules can be sufficiently distorted so that a simple hypothesis about the effective charge on each atom (e.g., each atom has $\delta z = 1/n$ in a molecule containing n atoms) gives very poor results. We have met with this problem in our calculations on 2-butene, 1,3-butadiene and acrolein. In these cases we could get some indication of the proper charge distribution from the spectroscopy of the molecule, and using these δz's the results of our calculations were quite good. Thus our approach has potentially one parameter, the proper charge distribution on the molecule. More work on larger systems may show how to get rid of this problem.

In closing this section on pseudopotentials and model potentials, we want to briefly discuss the kinds of solutions we expect. In solving our problems we use a variational approach, minimizing the quantity:

$$\frac{\langle \phi_n | T + V + V_p | \phi_n \rangle}{\langle \phi_n | \phi_n \rangle} \tag{21}$$

The solutions ϕ_n where n = v are our Rydberg orbitals, and we expect them to be smooth, with no nodes inside the core region. This causes no problems in the solution of equation (21). But what about the core orbitals ϕ_n where n = c? Is it possible that in solving equation (21) we will get core orbitals along with the valence orbitals we are seeking? For a pseudopotential defined by equation (16) the answer is yes! Weeks, Hazi and Rice[3] have attempted to define a pseudopotential which does not have this somewhat undesirable property, which they call variational collapse. But we see from our derivation of model potentials that a general definition of a pseudopotential like equation (16) is necessary if we want to make the transition to model potentials, and that variational collapse is always a possibility when working with model potentials. The fact that core solutions can appear in our calculations at times makes some of our results a little uncertain, but most of the time it is no trouble at all.

If we are using a pseudopotential V_p for which we know the functions F_c, we can calculate from equation (7) where these core states lie. Thus, for instance, for the Phillips-Kleinman pseudopotential of equation (17) we know that:

$$F_c = (E_v - E_c)\psi_c \tag{22}$$

where E_v is the lowest valence state eigenvalue. Substituting this into equation (7) for the core eigenvalue $\tilde{E}_c$, we see that:

$$\det\left|(E_{c'} - \tilde{E}_c)\delta_{c'c''} + (E_v - E_{c'})\langle\psi_{c'}|\psi_{c''}\rangle\right| = 0 \tag{23}$$

and thus that $\tilde{E}_c = E_v$ for every c. Thus all of the core states are degenerate with the lowest valence state for this particular potential. Furthermore, the degeneracy between E_v and $\tilde{E}_c$ means that we cannot solve uniquely for the coefficients β_c of the pseudo wavefunction, in fact the n-fold degeneracy of the above determinant means that the β_c may be taken completely arbitrarily, and that there are an infinity of solutions satisfying the Phillips-Kleinman pseudopotential. The general formula for this infinity of solutions is given by equation (11), where the coefficients β_c are arbitrary. It is interesting to note that this potential is the only pseudopotential with such sweeping properties, and that the usual pseudo or model potential is fairly well behaved.

In practice, in the cases of variational collapse which we have observed in our model potential calculations, the core states are usually separate and distinguishable from the valence states. These states usually have large negative energies lying below the valence states of interest. Sometimes, however, it can be a bit difficult to decide whether or not a state is the first member of a Rydberg series or the highest core state. Whenever this happens we must use the results of calculations on similar molecules and our "feeling" of how the calculation should behave, to separate appearance from reality.

References

1. For an extensive review of this early solid state work, see W. A. Harrison, Pseudopotentials in the Theory of Metals, Benjamin, New York (1966).
2. See W. A. Harrison, ibid.
3. See J. D. Weeks, A. Hazi and S. A. Rice, Adv. in Chem. Phys. 16, 283 (1969).
4. This proof is taken from J. Austin, V. Heine and L. J. Sham, Phys. Rev. 127, 276 (1962).
5. I. V. Abarenkov and V. Heine, Phil. Mag. 12, 529 (1965).
6. A. U. Hazi and S. A. Rice, J. Chem. Phys. 48, 495 (1968).

3. ATOMIC CALIBRATION

In the last section on Pseudopotentials and Model Potentials we explained how we write the model potential for a molecule as a sum of atomic potentials:

$$(1) \qquad V_M^{\text{molecule}} = \sum_{\text{atoms}} V_M^{\text{atom}}$$

Once these atomic model potentials have been independently determined from experimental atomic data we can use them to produce a parameter-free molecular model potential. What we want to do in this section is to calculate the atomic model potentials and calibrate them using experimental spectroscopic term values. In the next section on Molecular Calculations we will discuss the details of how these atomic model potentials are then used in calculating molecular Rydberg states.

The solution of the one-electron Schrödinger equation for an atomic Rydberg state with the atomic model potential V_M^{atom} of the last section is straightforward, writing:

$$(2) \qquad (-\tfrac{1}{2}\nabla^2 + V_M^{\text{atom}})\,\psi_E = E\psi_E$$

and putting $\psi_E = [R_E^{\ell}(r)/r]\,Y_{\ell m}(\theta, \phi)$ we see, upon using the definition of V_M^{atom}, that equation (2) splits up into two equations, namely:

$$(3) \qquad \frac{d^2\bar{R}_E^{\ell}}{dr^2} + \left[2(E - A) + \frac{\ell(\ell+1)}{r^2}\right]\bar{R}_E^{\ell} = 0 \qquad r \leq r_0$$

and

$$(4)\quad \frac{d^2\tilde{R}_E^{\ell}}{dr^2} + \left[2E + \frac{2}{r} - \frac{\ell(\ell+1)}{r^2}\right]\tilde{R}_E^{\ell} = 0 \qquad r \geqslant r_0$$

For a complete solution to our problem, we must find a solution valid in each region separately, with the property that at the point $r = r_0$, the values and the slopes of the two solutions are equal. In other words:

$$(5)\qquad R_E^{\ell}(r) = \begin{cases} \bar{R}_E^{\ell}(r) & r \leqslant r_0 \\ \tilde{R}_E^{\ell}(r) & r \geqslant r_0 \end{cases}$$

provided that at the point $r = r_0$ we have:

$$(6)\qquad \frac{d}{dr}\,\ell n\,\bar{R}_E^{\ell}(r) = \frac{d}{dr}\,\ell n\,\tilde{R}_E^{\ell}(r)$$

The solutions of equation (3) which vanish at $r = 0$ are simple rational functions in $\sin\sqrt{2|E-A|}\,r$, $\cos\sqrt{2|E-A|}\,r$, and $\sqrt{2|E-A|}$ or $\sin h\sqrt{2|E-A|}$ $\cos h\sqrt{2|E-A}\,r$, and $\sqrt{2|E-A|}$ depending on whether $(E - A)$ is positive or negative respectively. When $E - A = 0$, the solution of equation (3) with these boundary conditions is simply $r^{\ell+1}$. In particular if $\ell = 0$

$$(7)\quad \bar{R}_E^{\ell}(r) = \begin{cases} \sin\sqrt{2|E-A|}\,r & E - A > 0 \\ r & E - A = 0 \\ \sin h\sqrt{2|E-A|}\,r & E - A < 0 \end{cases}$$

Solutions of equation (4) are just the Coulomb functions which decay exponentially at large r. This can be expressed by the formula:[1]

$$(8) \qquad \tilde{R}_E^{\ell}(r) = {}^0U^{\ell}(r, E) + \gamma(n, \ell)\, {}^1U^{\ell}(r, E)$$

where:

$$(9) \qquad \gamma(n, \ell) = \frac{n^{2\ell+1}\, \Gamma(n - \ell) \tan (n - \ell - 1)\pi}{\Gamma(n + \ell + 1)}$$

$$n = 1/\sqrt{2|E|}$$

In the above formulae $\Gamma(n)$ is the Euler gamma function, and the functions ${}^0U^{\ell}(r, E)$ and ${}^1U^{\ell}(r, E)$ are the regular and irregular Coulomb wavefunctions. These functions, as well as the related functions:

$$(10) \qquad {}^0D^{\ell}(r, E) = r \frac{d}{dr} {}^0U^{\ell}(r, E);$$

$$ {}^1D^{\ell}(r, E) = r \frac{d}{dr} {}^1U^{\ell}(r, E)$$

have been tabulated for $\ell = 0, 1, 2$ over the range $-1.20 \leq E \leq -0.07$ Rydbergs and $2.0 \leq r \leq 8.3$ a.u. by Blume, Briggs and Brooks.[2] In addition to this, Kuhn[3] has given double power series expansions for these functions which converge for small negative values of the energy. Thus we were able to determine ${}^0U^{\ell}(r, E)$,

${}^1U^\ell(r, E)$, ${}^0D^\ell(r, E)$ and ${}^1D^\ell(r, E)$ for all negative values of the energy between $-1.2 \leq E \leq 0.0$ Rydbergs.

We can use equations (8) and (9) to prove our assertions about the behavior of $\tilde{R}^\ell_E(r)/r$ for small r which we made in the section on Rydberg Series to explain the creation of nodes at the origin, the interpretation of the quantum defect δ as a phase, etc. To do this we expand ${}^0U^\ell(r, E)$ and ${}^1U^\ell(r, E)$ in power series in r, valid for small r, i.e.:

$$(11) \qquad {}^0U^\ell(r, E) = r^\alpha \sum_{n=0}^{\infty} a_n r^n$$

$$ {}^1U^\ell(r, E) = r^\beta \sum_{n=0}^{\infty} b_n r^n$$

Putting these expressions into equation (4), and equating the coefficients of the powers of r equal to zero, we obtain:

$$(12) \quad {}^0U^\ell(r, E) =$$

$$\text{const } r^{\ell+1}\left\{1 - \frac{1}{(\ell+1)}r + \left[\frac{1}{(\ell+1)(\ell+3)} - \frac{E}{(\ell+3)}\right]r^2 + \cdots\right\}$$

$${}^1U^\ell(r, E) =$$

$$\text{const } r^{-\ell}\left\{1 + \frac{1}{\ell}r + \left[\frac{E}{(4\ell-1)} + \frac{1}{\ell(4\ell-1)}\right]r^2 + \cdots\right\}$$

It is clear that the first solution is regular at the origin, and that the second is irregular there. We note that the second solution

is not valid for $\ell = 0$. This means that the $\ell = 0$ solution has a higher order singularity at the origin than can be expressed by a simple n^{th} order pole $1/r^n$.

Using the above expressions, we can write $\tilde{R}^1_E(r)/r$ as:

$$(13)\quad \frac{\tilde{R}^1_E(r)}{r} \simeq \{r - \tfrac{1}{2}r^2 + (\frac{1}{6} - \frac{E}{4})r^3 + \cdots\} +$$

$$\text{const}\ \{\tan(\frac{1}{\sqrt{2|E|}} - 2)\pi\}\{\frac{1}{r^2} + \frac{1}{r} + (\frac{E}{3} - \frac{1}{3}) + \cdots\}$$

This function is just the un-normalized general hydrogen solution we were talking about in the Rydberg series section. It is clear that this function is infinite at the origin unless $|E| = 1/2n^2$, when it forms a node at the origin. The way in which the function approaches and recedes from the coordinate axis and reflects in the abscissa at the energies $|E| = 1/2(n + \frac{1}{2})^2$ is essentially determined by the factor $\tan(1/\sqrt{2|E|} - 2)\pi$. The existence of the outward moving nodes is established by the principle of continuity. Finally, the existence of periodic wave solutions and the phase interpretation of the quantum defect δ is suggested by the similarity of the hydrogen atom solutions for small r, together with the principle of continuity. Using all of these simultaneously we obtain the picture of $\tilde{R}^1_E(r)/r$, for small r, presented earlier.

Now that we have complete solutions for both $\bar{R}^\ell_E(r)$ and $\tilde{R}^\ell_E(r)$, obeying proper boundary conditions in their respective domains, we must join these functions together at the point $r = r_0$.

This cannot be done for every value of the energy E, but only at certain discrete values E_n. These values will be a function of the atomic parameter A and will represent the discrete energy spectrum $E_n(A)$ for an atom with the parameter A. As we have said before, to be physically meaningful, r_0 must be approximately 2.0 a.u. In our calculations we have taken $r_0 = 2.5$ a.u. This was done so that we could compare our results directly with similar calculations by Hazi and Rice.[4] The criterion that the functions $\bar{R}^{\ell}_E(2.5)$ and $\tilde{R}^{\ell}_E(2.5)$ must satisfy is, according to equation (6), that their logarithmic derivatives be equal. The logarithmic derivative of $\bar{R}^{0}_E(2.5)$ is:

$$(14)\quad \frac{d}{dr} \ln \bar{R}^{0}_E = \begin{cases} \sqrt{2|E-A|} \cot 2.5\sqrt{2|E-A|} & E-A>0 \\ 1/2.5 & E-A=0 \\ \sqrt{2|E-A|} \coth 2.5\sqrt{2|E-A|} & E-A<0 \end{cases}$$

Similarly, the logarithmic derivative of $\tilde{R}^{0}_E(2.5)$ is:

$$(15)\quad \frac{d}{dr} \ell n \tilde{R}^{0}_E = \frac{1}{r} \cdot \frac{{}^0D^0(2.5,E) + \gamma(n,\ell)\,{}^1D^0(2.5,E)}{{}^0U^0(2.5,E) + \gamma(n,\ell)\,{}^1U^0(2.5,E)}$$

These functions are plotted as a function of energy in Figures (1) and (2) respectively. Figure (1) is fairly straightforward, the different plots on the graph representing values of A. Figure (2) however needs some explanation. The most remarkable fact about this function is the presence of infinite discontinuities. These must come about every time the energy is such that a node passes

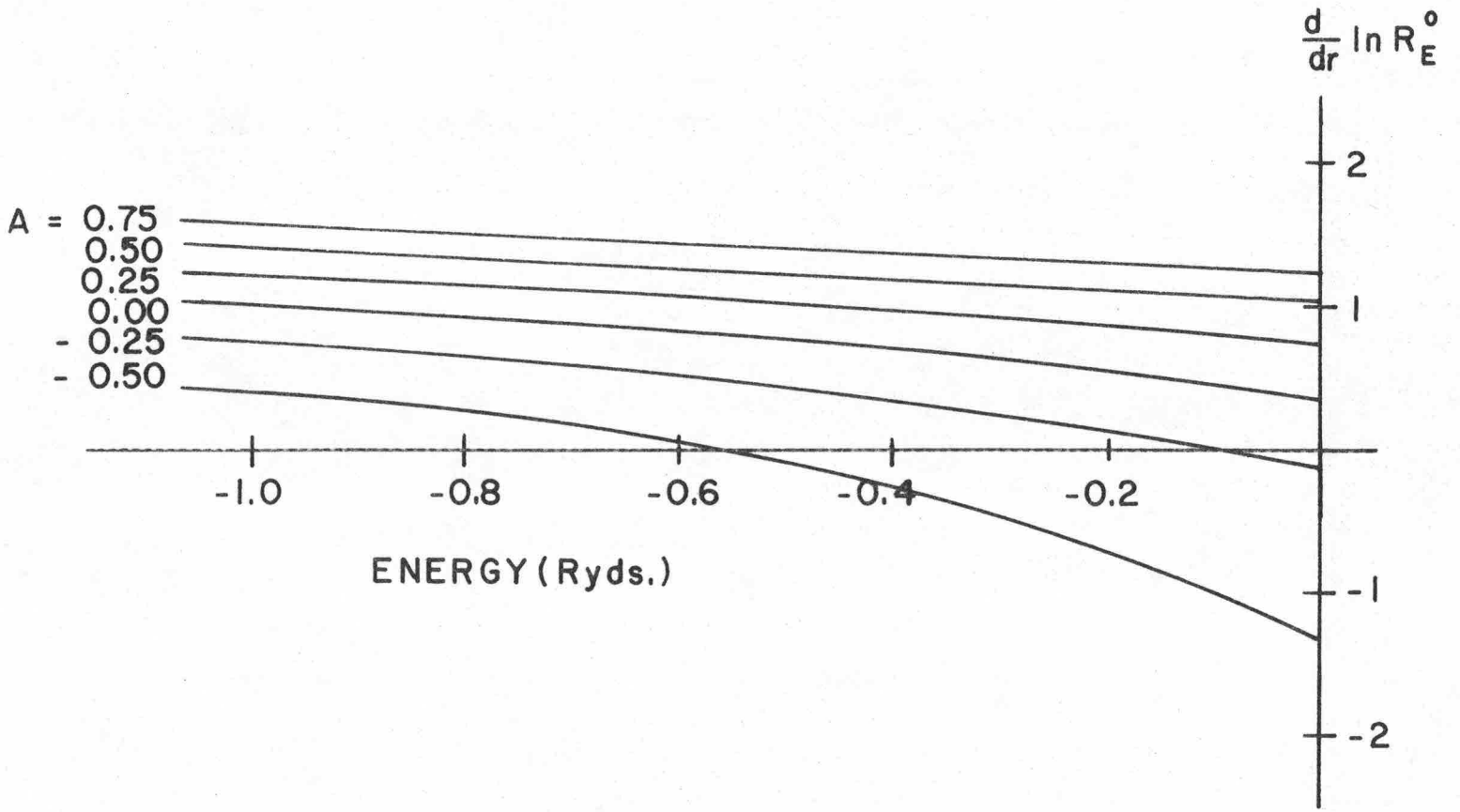


Figure 1. $\frac{d}{dr} \ln \bar{R}_E^o$ (2.5) as a Function of Energy

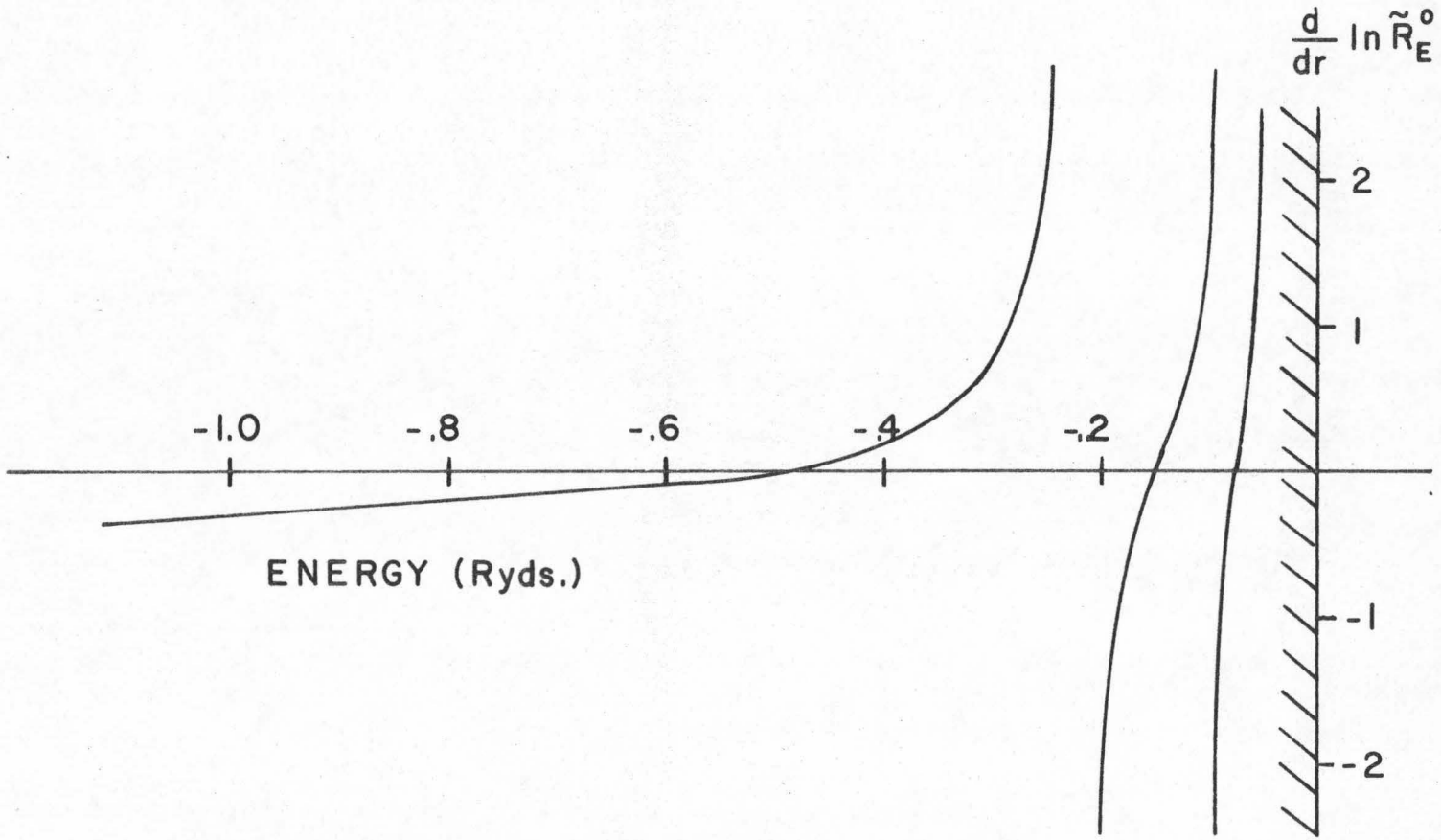


Figure 2. $\frac{d}{dr} \ln \bar{R}_E^o(2.5)$ as a Function of Energy

through the point $r_0 = 2.5$ a.u. Not all of the function $\frac{d}{dr} \ln \tilde{R}^0_E$ has been plotted on Figure (2). In the hatched region where $|E|$ is small the branches of the function crowd together with a frequency of roughly $1/n^2$ in the energy coordinate. This is impossible to represent on a graph.

In order to find the energy spectrum $E_n(A)$, we merely have to note the places where the curve of $\frac{d}{dr} \ln \bar{R}^0_E$ for a given A intersects the curve $\frac{d}{dr} \ln \tilde{R}^0_E$. The energies corresponding to these intersections then form the energy spectrum $E_n(A)$. Because the function $\frac{d}{dr} \ln \tilde{R}^0_E$ has the nature of a universal function and because it is so difficult to calculate, we give a more complete tabulation of it in Table 1. One can use these results to calibrate different atomic potentials from the ones we have treated here. It is evident from looking at Figure (2) that only the part for $-0.7 \leq E$ Rydbergs need be considered.

In the above, we have treated in detail the case of $\bar{R}^0_E(r)$ and $\tilde{R}^0_E(r)$. In principle we could use any $\bar{R}^{\ell}_E(r)$ to determine A. The A's determined by these different functions would then be slightly different, depending on the value of ℓ. In practice, we have restricted ourselves to $\ell = 0$. Once we have the spectrum $E_n(A)$ determined from the above functions, we compare this calculated spectrum with the experimentally known term values[5] of the atom we wish to calibrate. By calculating $E_n(A)$ for several values of A, we can interpolate to find an acceptable value of A for the atom we wish to represent. In Table (2) we list the energy spectra for several values of the parameter A measured in

Table 1

$\frac{d}{dr} \ln \tilde{R}^{o}_{E}$ as a function of E, for $r_0 = 2.5$ a.u.

E	$\frac{d}{dr} \ell n \tilde{R}^{o}_{E}$	E	$\frac{d}{dr} \ell n \tilde{R}^{o}_{E}$
-.700	-.33414	-.100	32.62618
-.600	-.21309	-.095	-3.44223
-.500	-.05653	-.090	-1.39588
-.400	.17819	-.085	-.69546
-.350	.36936	-.080	-.28684
-.300	.71416	-.075	.03778
-.280	.97362	-.070	.38012
-.260	1.45002	-.065	.90445
-.240	2.76303	-.060	2.71501
-.230	5.20690	-.058	8.92571
-.220	92.99086	-.056	-6.20680
-.210	-5.23922	-.054	-2.04998
-.200	-2.33908	-.052	-1.05932
-.190	-1.37637	-.050	-.56913
-.180	-.87180	-.048	-.23827
-.170	-.54101	-.046	.03902
-.150	-.06740	-.044	.32304
-.140	.15277	-.042	.69147
-.130	.41112	-.040	1.37894
-.120	.79442	-.038	4.69873
-.110	1.68647	-.036	-3.18654

Table 1 (Cont.)

E	$\frac{d}{dr} \ln \tilde{R}^{o}_{E}$
-.035	-1.51187
-.034	-.85259
-.033	-.46501
-.033	-.17942
-.031	.07080
-.030	.32921
-.029	.65139
-.028	1.17483
-.027	2.59673
-.026	-2.84150
-.025	-1.86150
-.024	-.70115
-.023	-.17925
-.022	.23309
-.021	.75914
-.020	2.23536

Rydbergs. For comparison, in Table (3) we have listed the experimentally observed spectra, measured in Rydbergs, for the atoms carbon, nitrogen and oxygen. This table has been constructed using the average of the ^1P and ^3P states with electronic configuration $(1s)^2(2s)^2(2p)(ns)$ for carbon, the average of the ^2P and ^4P states with electronic configuration $(1s)^2(2s)^2(2p)^2(ns)$ for nitrogen, and the average of the ^3S and ^5S states with electronic configuration $(1s)^2(2s)^2(2p)^3(ns)$ for oxygen. It will be remembered from the section on Rydberg series that this is the procedure for evaluating the term values for a non-closed shell atom.

We now only need to list the parameters which we have determined for the above atoms. Using a least squares fitting procedure we have decided on the parameters:

$$A_{carbon} \simeq .375 \text{ a.u.}$$

$$A_{nitrogen} \simeq .115 \text{ a.u.}$$

$$A_{oxygen} \simeq .045 \text{ a.u.}$$

The above values of A are given in atomic units rather than Rydbergs because our molecular program is scaled in terms of atomic units. One fact that should be noted, is that the results of molecular calculations with these parameters show that the above values can be changed by a factor of two or so with very little effect upon the resulting energies.

Table 2

$E_n(A)$, for $n = 3, 4, \cdots, 8$, $-.50 \leq A^a \leq .75$

n	A = -.50	A = -.25	A = 0.0	A = .25	A = .50	A = .75
3	.54[b]	.3694	.3091	.2846	.2717	.2642
4	.177	.1448	.1276	.1197	.1169	.1146
5	.088	.0762	.0691	.0659	.0642	.0632
6	.053	.0468	.0433	.0417	.0408	.0403
7	.035	.0317	.0297	.0288	.0283	.0280
8	.025	.0228	.0217	.0210	.021	.021

(a) A is measured in Rydbergs

(b) The last digit in each figure is not necessarily significant.

Table 3

Experimental Spectra for $\ell = 0$

n	Carbon	Nitrogen	Oxygen
3	.2744	.2996	.3149
4	.1157	.1227	.1274
5	.0702	.0674	.0690
6	.0392	.0425	.0432
7	.0280	.0296	.0296
8		.0222	.0215

References

1. I. V. Abarenkov and V. Heine, Phil. Mag 12, 529 (1965).
2. M. Blume, W. Briggs and H. Brooks, Tech. Rep. No. 260, Cruft Lab., Harvard University.
3. T. S. Kuhn, Quarterly of Applied Mathematics 9, 1 (1951).
4. A. Hazi and S. A. Rice, J. Chem. Phys. 48, 495 (1968).
5. C. E. Moore, Atomic Energy Levels, National Bureau of Standards (1949).

4. MOLECULAR CALCULATIONS

In this final section we describe the general mechanics of carrying out the program which we have outlined in earlier sections. We write a model potential for molecular Rydberg states $V_M^{molecule}$ as a sum of atomic model potentials:

$$(1) \qquad V_M^{molecule} = \sum_{atom} V_M^{atom}$$

and solve the resulting wave equation:

$$(2) \quad (-\frac{\hbar^2}{2m}\nabla^2 + V_M^{molecule})\psi_n^{Ryd} = E_n^{Ryd}\psi_n^{Ryd}$$

for the wavefunctions ψ_n^{Ryd} and corresponding energies E_n^{Ryd} of the molecular Rydberg states. Here we will limit ourselves to general questions about coordinate systems, basis functions, etc., which apply to all of our calculations. The remaining parts of this section will discuss individually the (1) symmetries, (2) geometries, (3) spectroscopy, (4) results of calculations, (5) interpretation of the optical spectrum and (6) electron impact data for each of the molecules for which we have calculated molecular Rydberg states.

The first point which we want to take up pertains to the method of choosing coordinates. In the following sections we have always taken the z axis to be the axis of highest symmetry in the molecule, except when explicitly stated otherwise. If the molecule, or the molecule minus its hydrogen atoms, is planar, then the y axis is taken in the plane and the x axis is out of the

plane. Again, there may be specific exceptions to the above general rules. Distances are in atomic units (~ .529 Å), and energy in hartree's (27.211 eV).

The general assumption used to fix the charge distribution is that an atom within a molecule containing n atoms has an effective charge of $\delta z = 1/n$. It is found that this assumptions works very well for both homonuclear and heteronuclear diatomics and triatomic molecules. For some of the larger molecules this assumption had to be altered. Specific details will be found in the sections describing the molecules individually.

In all cases the hydrogen atoms belonging to the molecule were disregarded. Besides the fact this assumption gave good results for all of the cases considered, it was tested specifically for ethylene. For ethylene the hydrogens were included using a model potential with A = 0.0 and δz = 0.04 at each of the hydrogen positions. Calculations on the $ns\sigma_g$ series with this molecular potential gave:

$$E_{3s} = 3.35, \quad E_{4s} = 1.48, \quad E_{5s} = .83$$

atomic units, in comparison to:

$$E_{3s} = 3.42, \quad E_{4s} = 1.49, \quad E_{5s} = .84$$

for the calculation neglecting the hydrogens. It is interesting to compare this difference with the difference caused by a change in the atomic parameters for the carbon atoms themselves. A

calculation with the hydrogen atoms absent, and a carbon parameter of $A_{carbon} = .205$ instead of .375, gave the $ns\sigma_g$ levels in ethylene as:

$$E_{3s} = 3.60, \quad E_{4s} = 1.55, \quad E_{5s} = .86$$

Thus, neither the neglect of the hydrogen atoms, nor small changes in the atomic parameters, have much of an effect on the results of our calculations.

We solved the Schrödinger wave equation (2) for our Rydberg orbitals ψ_n^{Ryd} by expanding these orbitals in a finite set of basis functions and variationally minizing the quantity:

$$(3) \qquad \frac{\langle \psi^{Ryd} | H | \psi^{Ryd} \rangle}{\langle \psi^{Ryd} | \psi^{Ryd} \rangle}$$

The program to do this was constructed from the one-electron part of a polyatom program, supplied to us by Dr. N. Winter. This program uses Gaussian basis functions of S and P symmetry. Although one has to use many such functions due to their incorrect asymptotic form, we feel that their other properties, expecially the ease of computation for orbitals of high n, and their general diffuseness, outweigh other considerations. By placing these functions at other than atomic centers, we were able to calculate Rydberg series of all except $nd\delta$ symmetry.

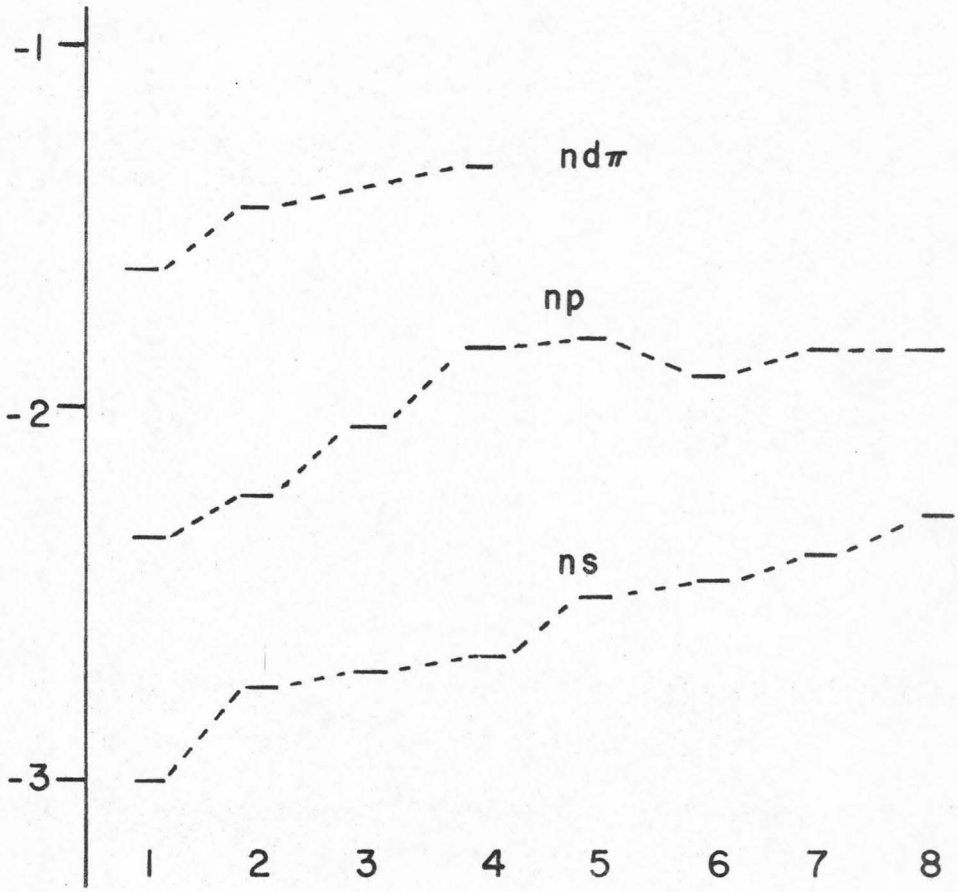
The actual calculations were very rapid. A complete set of calculations for a molecule, including Rydberg orbitals of ns, np

and nd symmetries, could be done in less than 30 minutes. The results are quite accurate, usually within 5-10% of available experimental results. It was not our intention to develop a scheme of high accuracy, but simply to illustrate that the use of model potentials can provide results of comparable accuracy to those of more tedious and elaborate approaches. It is obvious that direct SCF calculations of Rydberg states of large polyatomic molecules is presently not feasible, and it is an open question whether they would be worthwhile in any event.

We close this section with a comparison of our results with an experimental correlation for the term values of the lowest Rydberg states of each symmetry found by M. Robin[1] of Bell Laboratories. Figures (1) and (2) show Robin's experimental results and our results respectively for the term value of the lowest Rydberg state as a function of the size of the molecule. In both figures, the p and $d\pi$ levels are more or less constant, while the s level moves to higher energy with increasing size. The agreement is very good, and the correlation can be considered as established on the basis of both theory and experiment.

References

1. M. B. Robin, private communication.



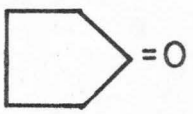
1 HCOH

2 CH_3COH

3 C_2H_5COH

4 CH_3COCH_3

5 $C_2H_5COC_2H_5$

6 

7 $CH_3COC(CH_3)_3$

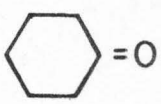
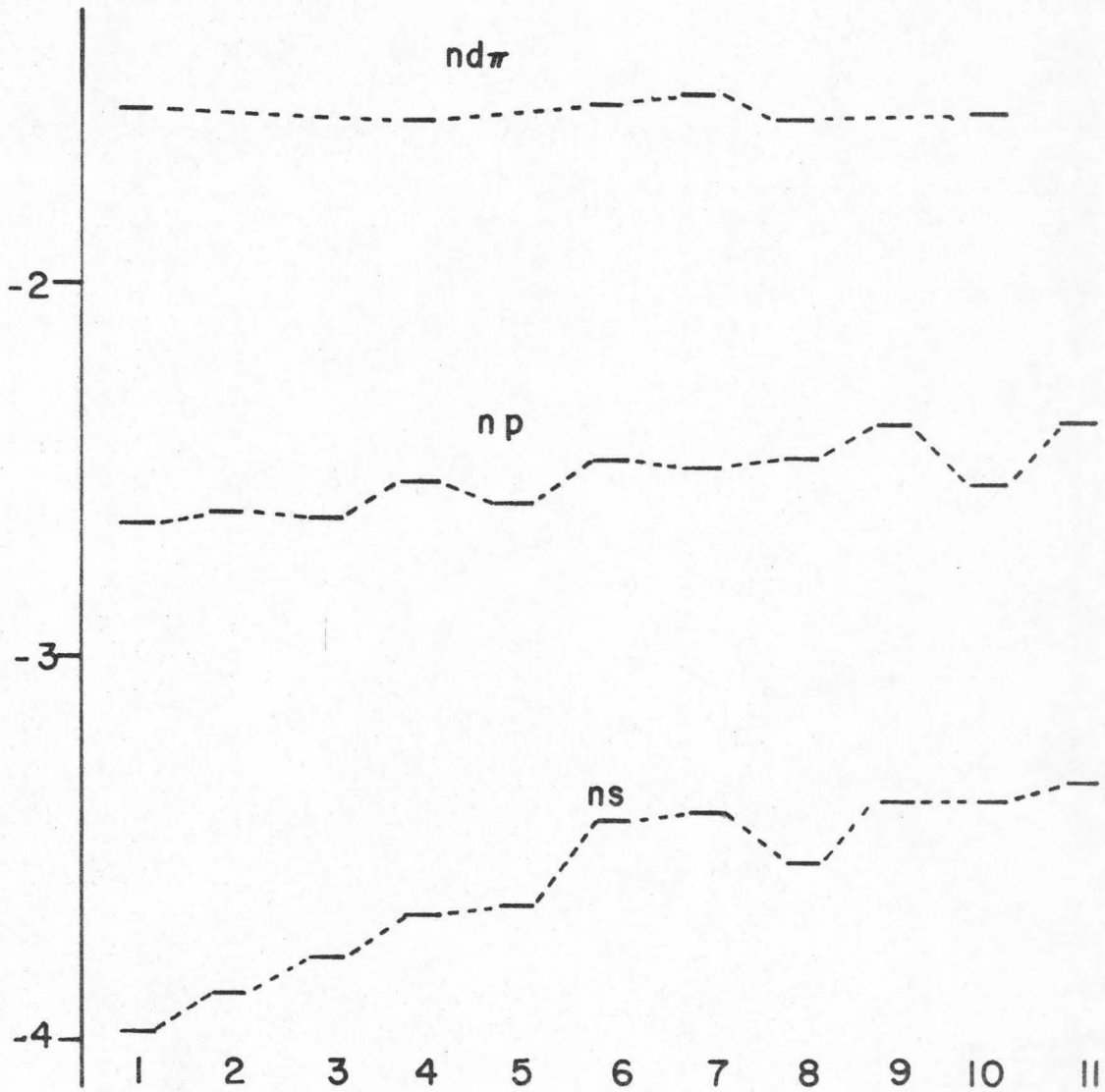
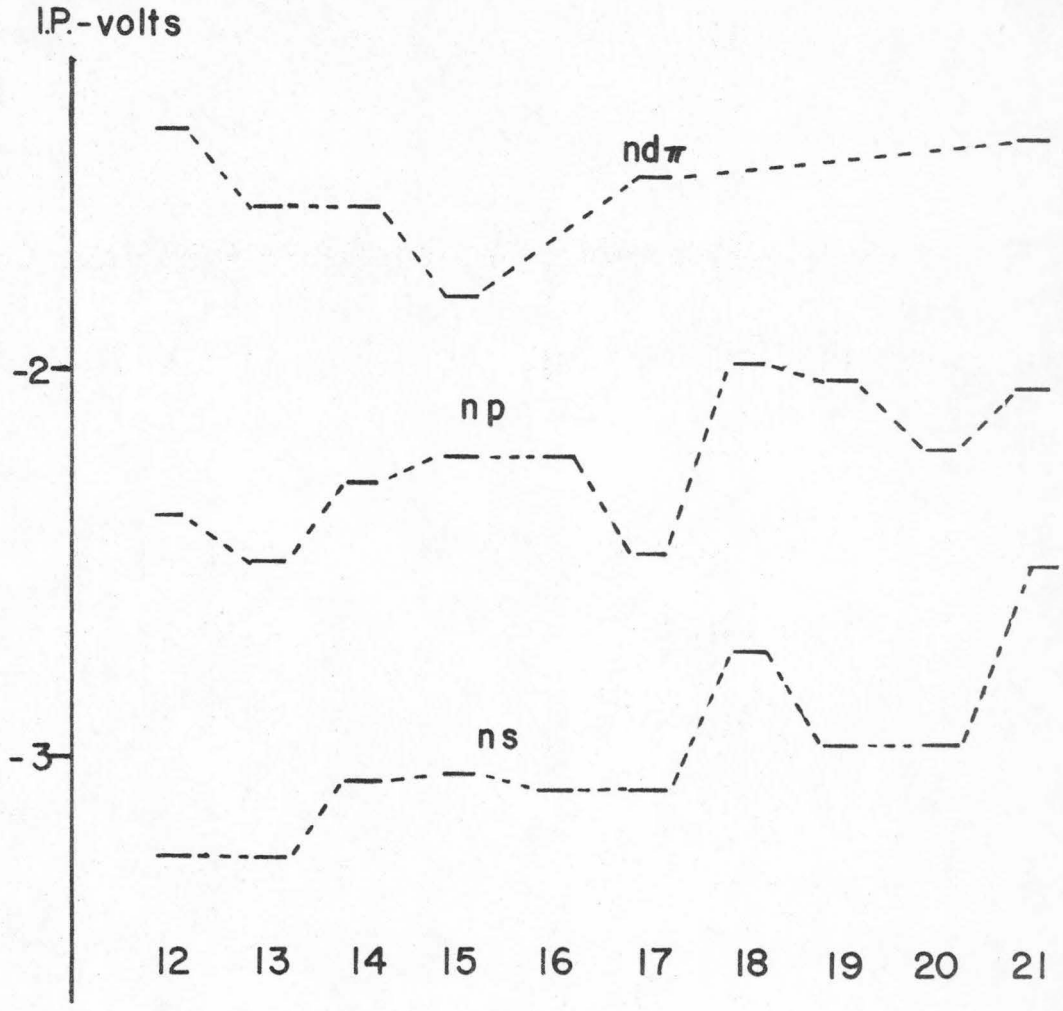
8 

Figure 1. Lowest Rydberg States as a Function of Molecular Size - M. B. Robin



1 O_2
2 NO
3 N_2
4 CO
5 CH_2O
6 C_2H_2
7 C_2H_4
8 N_2O
9 CO_2
10 CH_2O_2
11 CH_2N_2

Figure 2. Lowest Rydberg States as a Function of Molecular Size - T. C. Betts and V. McKoy



12	C_2H_2O	17	NO_2
13	C_2H_4O	18	C_4H_6
14	C_2H_6O	19	C_4H_8
15	C_3H_4	20	C_3H_4O
16	C_3H_6	21	C_6H_6

Figure 2 (cont.)

4.1 NITROGEN

Nitrogen, being a homonuclear diatomic, belongs of course to the group $D_{\infty h}$. The selection rules for dipole allowed transitions from the ground state are then:

$$^1\Sigma_u^+ \leftarrow \tilde{X} \qquad z \text{ transition}$$

$$^1\Pi_u \leftarrow \tilde{X} \qquad x, y \text{ transition}$$

Raman spectroscopy gives the nitrogen bond distance as 2.113 a.u. for the ground state $\tilde{X}$.

Orbital energies for nitrogen have been calculated by several investigators. The orbital energies as given by Nesbet[1] are reproduced below:

$1\sigma_g$	-15.69623
$1\sigma_u$	-15.69262
$2\sigma_g$	-1.48569
$2\sigma_u$	-0.78581
$3\sigma_g$	-0.64278
$1\pi_u$	-0.62261

We see that the $1\pi_u$ orbital is predicted in the Hartree-Fock model to lie above the $3\sigma_g$ orbital. Experimentally the opposite is observed,[2] the $1\pi_u$ orbital lies below the $3\sigma_g$ orbital. The electronic configuration of the ground state $\tilde{X}$ of nitrogen is then:

$$\{\text{core}\}\,(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2 \; - \; ^1\Sigma_g^+$$

where {core} denotes the orbitals:

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2 .$$

To account for the experimentally observed nitrogen spectrum, we have to consider the following Rydberg series. The series converging to the first ionization limit has the electronic configuration

$$\{\text{core}\}\,(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)(nR)$$

and the dipole allowed transitions will be $^1\Sigma_u^+(\sigma_u)$ and $^1\Pi_u(\pi_u)$, where the symmetries in parenthesis are the symmetries of the Rydberg orbitals.

The Rydberg series converging to the second ionization limit has the electronic configuration

$$\{\text{core}\}\,(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2(nR)$$

and the dipole allowed transitions will be $^1\Sigma_u^+(\pi_g)$ and $^1\Pi_u(\sigma_g)$.

Finally the electronic configurations of those Rydberg states converging to the third ionization limit are:

$$\{\text{core}\}\,(2\sigma_u)(1\pi_u)^4(3\sigma_g)^2(nR)$$

and the dipole allowed transitions are $^1\Sigma_u^+(\sigma_g)$ and $^1\Pi_u(\pi_g)$.

The optical spectrum of nitrogen has been extensively studied. Mulliken[3] states that the observed and predicted states are believed to be complete or very nearly so up to and including the second dissociation limit of the nitrogen molecule into ^4S and

^2D atoms just above 12 eV. Mulliken's tables give the details of the assignments of the nitrogen band spectrum, hence we limit ourselves to the Rydberg states here.

There is one and possibly two Rydberg series converging to the first ionization limit of nitrogen. This series is the well known Worley-Jenkins series. Since the series is composed of doublets, it has been suggested by Ogawa and Tanaka,[4] who have observed the series very carefully, that each component of the doublet might correspond to a different electronic transition. It is not possible as yet to either confirm or deny this hypothesis.

The two series have the formulae

(I) $125666.8 - R/(n + .3697 - .3459/n + .532/n - .960/n^4)^2$

and

(II) $125666.8 - R/(n + .3142 - .0404/n - .4289/n^4)^2$

corresponding to the term values:

(I)		(II)	
n	I.P. - ν	n	I.P. - ν
(2) p′	2.640	(2) c	2.646
(3) e	1.248	(3)	1.252
(3)	.731	(4)	.735
(4)	.481	(5)	.483
I.P. = 15.58 eV		I.P. = 15.58 eV	

There are two distinct series converging to the second ionization limit of nitrogen. The first of these is a doublet series, Worley's third series, whose components converge to the two components of the A $^2\Pi_u(N_2^+)$ ion, respectively. The second series is considerably weaker than the first. These series have the formulae:

Worley's third series

$136598 - R/(n - .0399 - .0258/n)^2$ $\qquad$ $134730 - R/(n - .1906 + .075/n)^2$

n		I.P. - ν	n	I.P. - ν
(2)	o′	3.587		
(3)		1.564 1.562	(3)	1.693
(4)		.870	(4)	.927
(5)		.554	(5)	.585
I.P. = 16.93 eV			I.P. = 16.70 eV	

Finally there are also two distinct Rydberg series converging to the third ionization limit of nitrogen. The first of these series is the well known Hopfield Rydberg series. The second series is much weaker and is observed on the wings of the Hopfield emission series. These two series are:

Hopfield series

$151233 - R/(n - .0701 - .0412/n)^2$		$151231 - R/(n + .1405 - .199/n)^2$	
n	I.P. - ν	n	I.P. - ν
(2)	3.872		
(3)	1.603	(3)	1.439
(4)	.885	(4)	.812
(5)	.563	(5)	.523
I.P. = 18.74 eV		I.P. = 18.74 eV	

The n = 2 member of the Hopfield series is not given by Ogawa and Tanaka,[4] it is however, listed by Mulliken[3] as a $^1\Sigma_u^+ [\{\text{core}\}(2\sigma_u)(1\pi_u)^4(3\sigma_g)^2(3s\sigma_g)]$ state.

In addition to these series there are many individual states which have been identified as Rydberg states. We discuss these states separately when we interpret the spectrum in the light of our calculations.

The results of our model calculations on nitrogen are as follows:

$ns\sigma_g$, $\delta = 1.1$	$np\sigma_u$, $\delta = .71$	$np\pi_u$, $\delta = .73$
3.80	2.60	2.63
1.61	1.23	1.26
.88	.72	.77
.53	.45	.47

$nd\sigma_g$, $\delta = .75$	$nd\pi_g$, $\delta = .06$
2.70	1.58
1.35	1.04
.79	.73
.40	

The basis sets used in these calculations are as follows. Gaussian basis functions were placed at the atomic centers, at the midpoint of the molecule and at centers 3.0 a.u. and 4.0 a.u. to either side of the atomic centers on the molecular axis. For the $ns\sigma_g$ and $np\sigma_u$ orbitals these functions were:

Center	Exponent	Type
Nitrogens	.45	s and p_z
	.15	
Midpoint	.05	s and p_z
	.0166	
	.0055	
	.0018	
	.0006	

For the $np\pi_u$ orbitals these functions were:

Center	Exponent	Type
Nitrogens	.15	p_x
	.05	
	.0166	
Extended Centers	.0055	p_x
(3.0 a.u.)	.0018	
	.0006	

For the $nd\sigma_g$ orbitals they were:

Center	Exponent	Type
Nitrogens	.45	p_z
	.15	
	.05	
Extended Centers	.0166	p_z
(3.0 a.u.)	.0055	
	.0018	
	.0006	

Finally for the $nd\pi_g$ orbitals they were:

Center	Exponent	Type
Nitrogens	.45	p_x
	.15	
	.05	
	.0166	

Center	Exponent	Type
Extended Centers	.0055	p_x
(4.0 a.u.)	.0018	
	.0006	
	.0002	

The interpretation of the optical Rydberg spectrum of nitrogen is fairly straightforward.

If we assume that the Worley-Jenkins series corresponds to two different electronic transitions, we see that they fit nicely with the $np\sigma_u$ and $np\pi_u$ series. It is not possible to distinguish which series is which, with the accuracy of the present calculations. The best fit, however, is with series I corresponding to the $np\sigma_u$ series and series II as $np\pi_u$. These states are then $^1\Sigma_u^+(\sigma_u)$ and $^1\Pi_u(\pi_u)$ states respectively.

Both of the series converging to the second ionization limit of nitrogen look like $ns\sigma_g$ series. This is also the feeling of Ogawa and Tanaka[4] who first observed these series. They assign to both series the electronic configuration $\{core\}\ (2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2$-$(ns\sigma_g)$ and consider the strong series to correspond to the singlet and the weak series the triplet state. We concur in this conclusion. The fact that the n = 2 member of the weak series is absent is understandable due to the forbidden character of the transition and the large number of bands in this region. We assign these states then as $^1\Pi_u(\sigma_g)$ and $^3\Pi_u(\sigma_g)$.

The Hopfield Rydberg series looks like another $ns\sigma_g$ series. We assign it as $^1\Sigma_u^+(\sigma_g)$. The other series which converges to the

third ionization limit of nitrogen fits reasonably well with an $nd\pi_g$ series. Ogawa and Tanaka[4] believe that the Hopfield series and this latter series should be assigned as $ns\sigma_g$ and $nd\sigma_g$. Our calculations definitely rule out the $nd\sigma_g$ possibility, while suggesting an $nd\pi_g$ assignment. We assign these states then as $^1\Pi(\pi_g)$. This completes the assignments of the observed Rydberg series. There are however many individual states which have been assigned as Rydberg states. In the following, we shall consider some of these states.

Our predicted term value of 3.80 eV for the $3s\sigma_g$ Rydberg state agrees well with the experimental values of 3.4 and 3.71 eV for the $^1\Sigma_g^+$ $[\{core\}(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)(3s\sigma_g)]$ and $^3\Sigma_g^+$ $[\{core\}(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)(3s\sigma_g)]$ states arising from a $3\sigma_g \rightarrow 3s\sigma_g$ transition and 3.89 eV for the $^1\Sigma_u^+$ $[\{core\}(2\sigma_u)(1\pi_u)^4(3\sigma_g)^2(3s\sigma_g)]$ state arising from a $2\sigma_u \rightarrow 3s\sigma_g$ transition.

In addition to the Worley-Jenkins series, there are other $np\sigma_u$ series observed in the nitrogen spectrum. There is a D $^3\Sigma_u^+$ $[\{core\}(2\ _u)^2(1\pi_u)^4(3\sigma_g)(4p\sigma_u)]$ state at 2.95 eV and another y $^1\Pi_g[\{core\}(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2(4p\sigma_u)]$ state at 2.11 eV. These values are consistent with our calculations.

The calculated term value for the lowest member of the $nd\sigma$ series is 2.70 eV. Mulliken[5] has suggested that the n $^1\Sigma_u^+$ state at 13.98 eV above the ground state of N_2 may be a member of the $nd\sigma_g$ series with configuration $\{core\}(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)(nd\sigma_g)$. This state then has a term value of 2.71 eV in very good

agreement with our predicted term value of 2.70 eV for this $nd\sigma_g$ Rydberg state.

Besides the Worley-Jenkins series, other $np\pi_u$ states have been observed in nitrogen. For instance the $^1\Pi_u$ $[\{core\}(2\sigma_u)^2-(1\pi_u)^4(3\sigma_g)(3p\pi_u)]$ and $^3\Pi_u$ $[\{core\}(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)(3p\pi_u)]$ states have been identified at 2.11 and 2.40 eV respectively. Also the z $^1\Delta_g$ $[\{core\}(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2(3p\pi_u)]$ and x $^1\Sigma_g^-$ $[\{core\}(2\sigma_u)^2-(1\pi_u)^3(3\sigma_g)^2(3p\pi_u)$ states are observed at 2.02 and 2.29 eV respectively. While these states are not in as good agreement with our calculations as the Worley-Jenkins series, they are reasonable values. This is so, because we expect these lowest members to deviate more than the higher members from their expected positions.

Finally no other $nd\pi_g$ state has been observed other than those of the series converging to the $^2\Sigma_u^+$ (N_2^+) ion of nitrogen.

The calculated term values for the Rydberg orbitals given above agree very well with those obtained by Lefebvre-Brion and Moser[6] by direct Hartree-Fock calculations. For example, some term values obtained from their Tables III-V give 3.68 and 1.68 eV for the $3s\sigma_g$ and $4s\sigma_g$ members of the $ns\sigma_g$ series; 2.48, 1.18 and .68 eV for the members of the $np\sigma_u$ series; and 2.48, 1.08 and .58 eV for the $3p\pi_u$, $4p\pi_u$ and $5p\pi_u$ members of the $np\pi_u$ series. The term values for the higher members of the Rydberg series can be obtained much more economically by our procedure than by direct Hartree-Fock calculations.

The electron impact spectrum of nitrogen has been observed by Lassettre, et al.,[7] and by Geiger and Stickel.[8] The spectrum of Geiger and Stickel is reproduced in Figure 1. We see that it exhibits considerable similarities to the optical spectrum but shows striking deviations in the range 12.8-14.5 eV where the intensity of the electron energy loss spectrum is much greater than that of the optical spectrum. This difference has been interpreted as due to the close lying transitions $p\ ^1\Sigma_u^+ \leftarrow \tilde{X}$ and $c\ ^1\Pi_u \leftarrow \tilde{X}$ being perturbed by the $c'\ ^1\Sigma_u^+$ and $b'\ ^1\Sigma_u^+$, and $b\ ^1\Pi_u$ states respectively. In the spectrum we can see the Worley-Jenkins series, Worley's third series and traces of the Hopfield series.

Finally, we want to compare our results on nitrogen with those of Lindholm.[9] We agree on the assignment of the series converging to the first ionization limit. We likewise agree with those converging to the second ionization limit with the exception of the series which we have identified as $^3\Pi_u$. Lindholm feels that the intensity of this series is too great for it to be a triplet series, and he assigns it as an $nd\sigma_g$ series. Our calculations show that an $nd\sigma_g$ should have a quantum defect $\delta \approx .75$ which does not agree at all with Lindholm's assignment. Finally, Lindholm assigns the two series converging to the third ionization limit of nitrogen as $ns\sigma_g$ and $nd\pi_g$ but just oppositely to the way we assign them.

In closing we note that Codling[10] has observed one and perhaps two members of what may be a Rydberg series of the $C\ ^2\Sigma_u^+ (N_2^+)$ ion. These states at 22.12 and 22.76 eV would have a

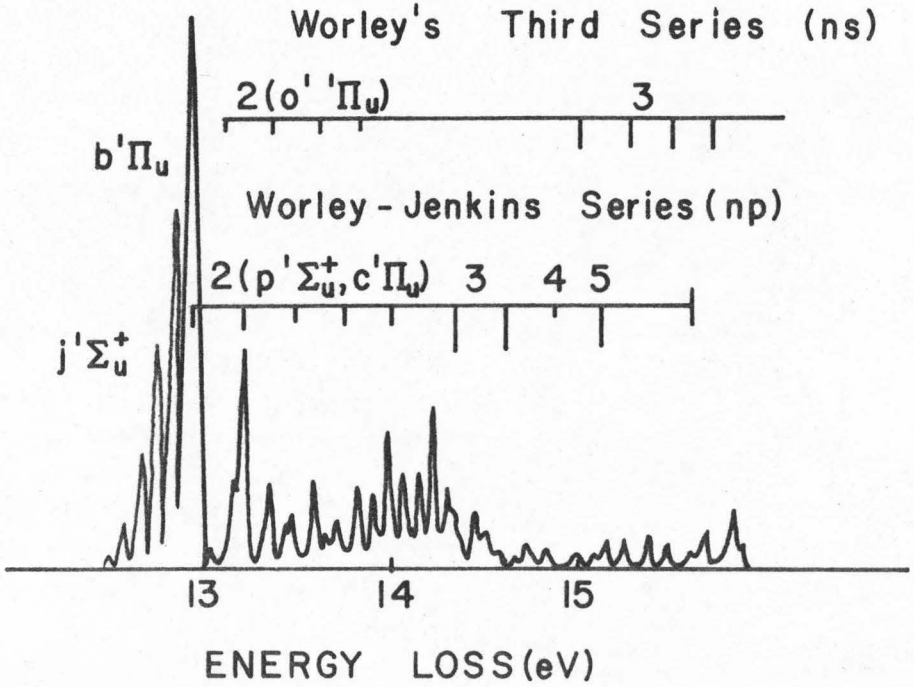


Figure 1. Electron Impact Spectrum of Nitrogen

quantum defect $\delta \approx .95$. Both Lindholm and we agree in assigning them as part of an $ns\sigma_g$ series, and hence as $^2\Sigma_u^+ (\sigma_g)$ states.

References

1. R. K. Nesbet, J. Chem. Phys. 40, 3619 (1964).
2. G. Herzberg, Molecular Spectra and Molecular Structure. I. Diatomic Molecules, Van Nostrand, 1967, p. 343.
3. R. S. Mulliken, "The Threshold of Space," Pergamon Press, Inc., New York (1957), p. 169.
4. M. Ogawa and Y. Tanaka, Can. J. Phys. 40, 1593 (1962).
5. R. S. Mulliken, ibid., p. 167.
6. H. Lefebvre-Brion and C. M. Moser, J. Chem. Phys. 43, 1394 (1965).
7. E. N. Lassettre, A. Skerbele, M. A. Dillon and K. J. Ross, J. Chem. Phys. 48, 5066 (1968).
8. J. Geiger and W. Stickel, J. Chem. Phys. 43, 4535 (1965).
9. E. Lindholm, Arkin För Fysik 40, 111 (1969).
10. K. Codling, Astrophys. J. 143, 552 (1966).

4.2 OXYGEN

Molecular oxygen is a homonuclear diatomic belonging to the group $D_{\infty h}$. The selection rules for dipole allowed transitions from the ground state are:

$$^3\Sigma_u^- \leftarrow \tilde{X} \qquad z \text{ transition}$$

$$^3\Pi_u \leftarrow \tilde{X} \qquad x, y \text{ transition}$$

The oxygen bond distance in the ground state has been determined as 2.282 a.u.

Orbital energies for oxygen have been calculated by several investigators, the restricted Hartree-Fock values are:[1]

$1\sigma_u$	-20.7722
$1\sigma_g$	-20.7717
$2\sigma_g$	- 1.5229
$2\sigma_u$	- 1.1679
$3\sigma_u$	- 0.6655
$1\pi_u$	- 0.6421
$1\pi_g$	- 0.6074

Herzberg[2] gives the electronic configuration of the ground state $\tilde{X}$, in agreement with the Hartree-Fock result, as:

$$\{\text{core}\}\,(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2 \; - \; ^3\Sigma_g^-$$

where {core} represents the orbitals:

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2 .$$

Thus, the Rydberg series converging to the first ionization limit of oxygen [i.e., the $X\ ^2\Pi_g\ (O_2^+)$ ion] has the electronic configuration:

$$\{core\}\ (2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)(nR)$$

and the dipole allowed transitions from the ground state will be $^3\Sigma_u^-\ (\pi_u)$ and $^3\Pi_u\ (\sigma_u)$, where the symmetries in parentheses are the symmetries of the Rydberg orbitals.

The electronic configuration of the Rydberg states converging to the $a\ ^4\Pi_u$ and $A\ ^2\Pi_u$ oxygen O_2^+ ions will be:

$$\{core\}\ (2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^3(1\pi_g)^2(nR)$$

and the dipole allowed transitions will be $^3\Sigma_u^-\ (\pi_g)$ and $^3\Pi_u\ (\sigma_g)$.

The electronic configuration of the Rydberg states converging to the $b\ ^4\Sigma_g^-$ and $B\ ^2\Sigma_g^-$ oxygen O_2^+ ions will be:

$$\{core\}\ (2\sigma_u)^2(3\sigma_g)(1\pi_u)^4(1\pi_g)^2(nR)$$

and the dipole allowed transitions will be $^3\Sigma_u^-\ (\sigma_u)$ and $^3\Pi_u\ (\pi_u)$.

Finally, the electronic configuration of the Rydberg states converging to the $c\ ^4\Sigma_u^-$ oxygen O_2^+ ion will be:

$$\{core\}\ (2\sigma_u)(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2(nR)$$

and the dipole allowed Rydberg transitions will be $^3\Sigma_u^-\ (\sigma_g)$ and $^3\Pi_u\ (\pi_g)$.

The optical spectrum of oxygen has been well studied. In the following we shall deal only with the observed Rydberg series and states which are believed to be Rydberg states.

There is no Rydberg series which is observed to converge to the first ionization limit of oxygen. However, Tanaka[3] has observed two progressions starting at 77321 cm^{-1} and 79967 cm^{-1} respectively which he suspects might be the first members of two Rydberg series. If we take the ionization limit of X $^2\Pi_g$ (O_2^+) as 12.06 eV, then these states would lie 2.48 and 2.15 eV below the ionization limit respectively.

Price and Collins[4] have observed two progressions converging to the a $^4\Pi_u$ (O_2^+) ion which they believe to be the first two members of a Rydberg series converging to this ion. These progressions start at 99630 cm^{-1} and 117200 cm^{-1}, and are called by them H and I respectively. Putting these values into the Rydberg formula the two states are found to lie 3.80 and 1.62 eV below the ionization limit at 130,000 cm^{-1} (16.15 eV). Price and Collins[4] observed two other progressions H′ and I′ at 101400 cm^{-1} and 118500 cm^{-1} respectively, which lie 3.71 and 1.60 eV below an ionization limit of 131,400 cm (16.29 eV). They postulate that these two states are the first two members of another Rydberg series different from the first series.

Price and Collins[4] have observed yet again two more progressions which may be the first two members of another Rydberg series. This series converges to the A $^2\Pi_u$ (O_2^+) ion. These progressions begin at 104470 cm^{-1} and 121064 cm^{-1} respectively

and are 3.83 and 1.77 eV below the ionization limit at 16.78 eV. They are designated as M and N.

As we have seen at wavelengths longer than about 850 Å only progressions of bands belonging to states which may be parts of Rydberg series are observed. Below this region complete Rydberg series have been observed. Kosino and Tanaka[5] have observed both a strong and a weak Rydberg series converging to the b $^4\Sigma_g^-$ (O_2^+) ion. These series are:

Strong series $146568 - R/(n - .67)^2$		Weak series $146570 - R/(n - .55)^2$	
n	I.P. - ν	n	I.P. - ν
(4)	1.239	(4)	1.133
(5)	.724	(5)	.672
(6)	.478	(6)	.445
I.P. = 18.17 eV		I.P. = 18.17 eV	

They also observed a strong and a weak Rydberg series converging to the B $^2\Sigma_g^-$ (O_2^+) ion. These series are:

Strong series $163702 - R/(n - .70)^2$		Weak series $163700 - R/(n - .55)^2$	
n	I.P. - ν	n	I.P. - ν
(4)	1.261		
(5)	.737		
(6)	.484	(6)	.455
I.P. = 20.29 eV		I.P. = 20.29 eV	

Finally, Codling and Madden[6] have observed three Rydberg series converging to the c $^4\Sigma_u^-$ (O_2^+) ion. Two of these series are of strong intensity and the third is weak. They are:

$198125 - R/(n - .19)^2$

n	I.P. - ν
(3)	1.700
(4)	.934
(5)	.589

I.P. = 24.56 eV

$198125 - R/(n - .98)^2$

n	I.P. - ν
(3)	3.702
(4)	1.485
(5)	.834
(6)	.534

I.P. = 24.56 eV

Weak series

$198125 - R/(n - .02)^2$

n	I.P. - ν
(4)	1.493
(5)	—
(6)	.541

I.P. = 24.56 eV

In general the members of the weak series lie approximately 50 cm^{-1} to the low energy side of the second strong Rydberg series above. Codling and Madden[6] suggest that this series either represents the spin orbit splitting of the strong series or the analogous quintet series to the triplet strong series.

The results of model calculations on oxygen are as follows:

$ns\sigma_g$, $\delta = 1.15$	np, $\delta = .74$	$nd\sigma_g$, $\delta = .80$	$nd\pi_g$, $\delta = .04$
3.97	2.64	2.82	1.55
1.67	1.25	1.34	1.02
.90	.73	.72	.55
.53	.45		

In the above table the $np\sigma_u$ and $np\pi_u$ results are so similar, they are simply denoted by np.

The basis sets used in these calculations are as follows. Gaussian basis functions were placed at the atomic centers, at the midpoint of the molecule, and at centers 3.0 a.u. to either side of the atomic centers on the molecular axis. For the $ns\sigma_g$ and $np\sigma_u$ orbitals these functions were:

Center	Exponent	Type
Oxygens	.45	s and p_z
	.15	
Midpoint	.05	s and p_z
	.0166	
	.0055	
	.0018	
	.0006	

For the $np\pi_u$ and $nd\pi_g$ orbitals the functions were:

Center	Exponent	Type
Oxygens	.15	p_x
	.05	
	.0166	
Extended Centers	.0055	p_x
	.0018	
	.0006	

Finally for the $nd\sigma_g$ orbitals they were:

Center	Exponent	Type
Oxygens	.45	p_z
	.15	
	.05	
Extended Centers	.0166	p_z
	.0055	
	.0018	
	.0006	

The interpretation of the optical Rydberg spectrum of oxygen goes as follows.

The progression observed by Tanaka at 2.48 eV below the first ionization limit is in reasonable agreement with a 3p Rydberg state, either $3p\sigma_u$ or $3p\pi_u$. This state is then either $^3\Pi$ (σ_u) or $^3\Sigma_g^-$ (π_u). The other progression observed at 2.15 eV below the ionization limit, despite its large deviation from the calculated

value, is probably another 3p state. We assign it as $^3\Pi\ (\sigma_u)$ or $^3\Sigma_g^-\ (\pi_u)$ also.

All of the progressions observed by Price and Collins are in good agreement with $ns\sigma_g$ series. This includes the H and I progressions and the H′ and I′ progressions converging to the a $^4\Pi_u\ (O_2^+)$ ion as well as the M and N progressions converging to the A $^2\Pi_u\ (O_2^+)$ ion. They all appear to be $3s\sigma_g$ and $4s\sigma_g$ states, and we assign them as $^3\Pi_u\ (\sigma_g)$.

When we get away from progressions and into complete series we are on firmer ground. Both the strong and weak series observed by Kosino and Tanaka[5] converging to the b $^4\Sigma_g^-\ (O_2^+)$ ion appear to be np series. Again, the strong and weak series converging to the B $^2\Sigma_g^-\ (O_2^+)$ ion observed by these authors also appear to be np series. Furthermore, the two strong series seem to correspond to the same Rydberg orbital as well as do the two weak series. We cannot decide which is $np\sigma_u$ and which is $np\pi_u$ on the basis of our calculations and therefore assign them as $^3\Sigma_u^-\ (\sigma_u)$ and $^3\Pi_u\ (\pi)$.

The two strong Rydberg series observed by Codling and Madden[6] seem to be $nd\pi_g$ and $ns\sigma_g$ series. The series with quantum defect $\delta = .19$ agrees reasonably well with either assignment, but because of the absence of an $n = 2$ member we must assign it as $nd\pi_g$ and the state as $^3\Pi_u\ (\pi_g)$. The other series with quantum defect $\delta = .98$ also agrees with both series, but the presence of an $n = 3$ member identifies it as $ns\sigma_g$ and hence $^3\Sigma_u^-\ (\sigma_g)$.

Thus the various Rydberg states of oxygen, though difficult to find and identify experimentally, are easily interpreted by our calculations. On the computational side, our calculations are also in good agreement with the more extensive treatment of Leclercq.[7]

The electron impact spectrum of oxygen has been measured by Lassettre[8] and co-workers. Their spectrum, together with our assignments, are given in Figure 1. It is clear that the electron impact spectrum resembles the optical spectrum fairly closely. One important difference, however, is the clarity with which the np states converging to the first ionization limit stand out. We are able to pick out the n = 3, 4 and 5 members of this series in the electron impact spectrum, whereas in the optical spectrum we could only find the first member.

It remains for us to compare our results with the predictions of Lindholm.[9] In identifying the various progressions observed in oxygen Lindholm and we differ as to how the progressions are to be arranged, but agree in which Rydberg series they must represent.

When we come to the interpretation of actual Rydberg series, we agree almost completely. We agree on the assignment of the series converging to the b $^4\Sigma_g^-$ and B $^2\Sigma_g^-$ (O_2^+) ions. We also agree with Lindholm's assignment of the nsσ_g series converging to the c $^4\Sigma_u^-$ (O_2^+) ion. The only disagreement we can find is with his assignment of ndσ_g for the other series converging to the c $^4\Sigma_u^-$ (O_2^+) ion. Our calculations show that this assignment is untentable and should be replaced by ndπ_g.

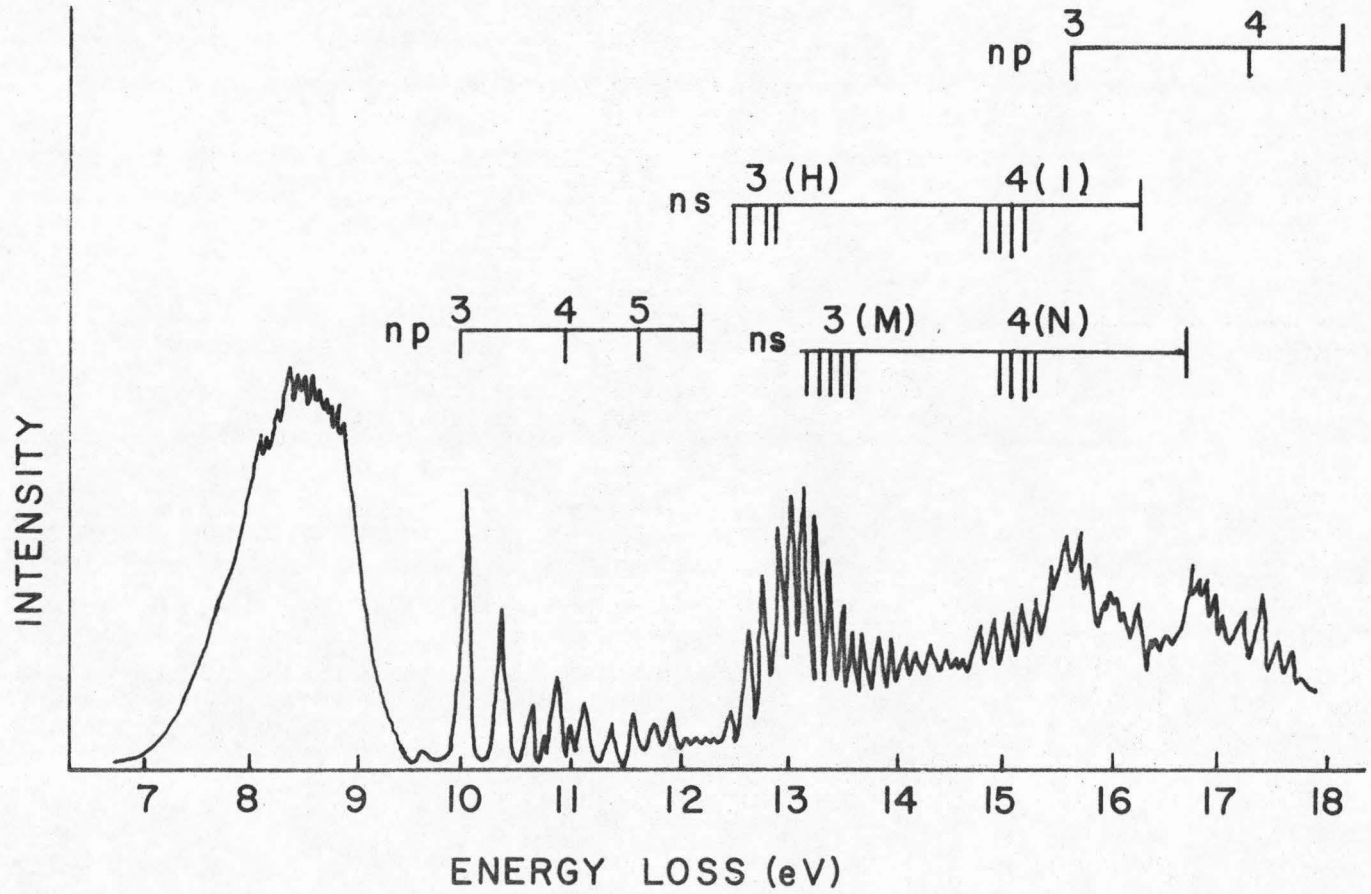


Figure 1. Electron Impact Spectrum of Oxygen

It should be mentioned that Lindholm attempts to assign several more states than we have. We have not considered the evidence complete enough to make these assignments.

References

1. Data supplied by John Rose, who assures us that these results are not whizzies.
2. G. Herzberg, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules, Van Nostrand Co., New York (1967), p. 343.
3. Y. Tanaka, J. Chem. Phys. 20, 1728 (1952).
4. W. C. Price and G. Collins, Phys. Rev. 48, 714 (1935).
5. K. Kosino, Y. Tanaka, J. Chem. Phys. 48, 4859 (1968).
6. K. Codling and R. P. Madden, J. Chem. Phys. 42, 3935 (1965).
7. J. Leclercq. Ann. de Astrophysique 30, 93 (1967).
8. E. N. Lassettre, A. Skerbele, M. A. Dillon, and K. J. Ross, J. Chem. Phys. 48, 5066 (1968).
9. E. Lindholm, Arkiv. För Fysik 40, 117 (1969).

4.3 NITRIC OXIDE

Nitric oxide is a heteronuclear diatomic belonging to the group $C_{\infty v}$. The selection rules for dipole allowed transitions from the ground state are:

$$^2\Pi \leftarrow \tilde{X} \qquad z \text{ transition}$$

$$^2\Sigma^+ \leftarrow \tilde{X} \qquad x, y \text{ transitions}$$

The internuclear distance has been measured as 2.176 a.u. for the ground state $\tilde{X}$.

Orbital energies for nitric oxide have been calculated by several authors. Those given by Brion, Moser, and Yamazaki[1] are typical and are given below:

1σ	-20.6130	-20.6185
2σ	-15.6206	-15.6450
3σ	-1.5227	-1.4862
4σ	-0.8656	-0.8589
1π	-0.5427	-0.5593
5σ	-0.5427	-0.5353
2π	-0.3304	-0.3358
E_T	-128.883	-128.737

Thus the electronic configuration for nitric oxide is:

$$\{\text{core}\}\,(5\sigma)^2(1\pi)^4(2\pi) \; - \; ^2\Pi$$

where {core} represents the orbitals:

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2$$

The Rydberg states converging to the first ionization limit of nitric oxide will have the electronic configuration:

$$\{\text{core}\}\,(5\sigma)^2(1\pi)^4(\text{nR})$$

and the dipole allowed transitions from ground state will be $^2\Pi\ (\pi)$ and $^2\Sigma^+\ (\sigma)$, where the symmetries in parenthesis are the symmetries of the Rydberg orbitals.

The Rydberg states converging to the second and third ionization limits will have the electronic configuration:

$$\{\text{core}\}\,(5\sigma)^2(1\pi)^3(2\pi)(\text{nR}).$$

Finally the Rydberg states converging to the fourth ionization limit will have the electronic configuration:

$$\{\text{core}\}\,(5\sigma)(1\pi)^4(2\pi)(\text{nR})$$

and the dipole allowed transitions will be $^2\Pi\ (\sigma)$ and $^2\Sigma^+\ (\pi)$.

The optical Rydberg spectrum of nitric oxide shows numerous states which can be fitted into Rydberg series converging to the first ionization limit at 9.27 eV. As measured by Lagerquist and Miescher,[2] these states are:

	$9.27 - \nu$
A	3.281
E	1.755
S	.949
C	2.806
K	1.301
D	2.682
M	1.256
F	1.580
H′	1.502
H	1.497

Furthermore there is a Rydberg series, α, converging to the second ionization limit of nitric oxide. As observed by Huber[3] the formula for this series is:

$$114680 - R/(n - 1.10)^2$$

n	I.P. $- \nu$
(3)	4.013
(4)	1.599
(5)	.923
(6)	.566
	I.P. = 14.21 eV

Huber[3] has also observed the Rydberg series, β, converging to the third ionization limit of nitric oxide. It is a doublet series

with the formula:

$$135530 - R/(n - .67)^2$$

n	I.P. - ν
(3)	2.985
	2.740
(4)	1.514
	1.261
(5)	.983
	.737
(6)	.726
	.483

I.P. = 16.80 eV

Finally, Huber[3] has observed the Rydberg series, γ, converging to the fourth ionization limit of nitric oxide. It is another doublet series with the formula:

$$147830 - R/(n - .78)^2$$

n	I.P. - ν
(3)	2.837
	2.630
(4)	1.319
	1.116
(5)	.767
	.560

n	I.P. - ν
(6)	.500
	.295
	I.P. = 18.32 eV

The results of model calculations on nitric oxide are as follows:

nsσ, δ = 1.13	npσ, δ = .72	ndσ, δ = .78
3.88	2.62	1.31
1.64	1.24	.70
.89	.72	
.53	.45	

ndπ, δ = .74	ndπ, δ = .06
2.65	1.58
1.28	1.03
.74	.55
.46	

The basis sets used in these calculations were as follows. Gaussian basis functions were placed at the atomic centers, at the midpoint of the molecule and at centers 3.0 a.u. to either side of the atomic centers on the molecular axis. For the nsσ and npσ orbitals these functions were:

Center	Exponent	Type
Nitrogen, Oxygen	.45	s and p_z
	.15	
Midpoint	.05	s and p_z
	.0166	
	.0055	
	.0018	
	.0006	

For the $np\pi$ and $nd\pi$ orbitals these functions were:

Center	Exponent	Type
Nitrogen, Oxygen	.15	p_x
	.05	
	.0166	
Extended Centers	.0055	p_x
	.0018	
	.0006	

Finally for the $nd\sigma$ orbitals they were:

Center	Exponent	Type
Nitrogen, Oxygen	.45	p_z
	.15	
	.05	

Center	Exponent	Type
Extended Centers	.0166	p_z
	.0055	
	.0018	
	.0006	

The interpretation of the optical spectrum of nitric oxide goes as follows. The states A, E and S fit nicely with an nsσ series converging to the first ionization limit. These states would then be $^2\Sigma^+$ (σ) states. The states C and K are in reasonable agreement with an npπ series converging to the same limit. We assign these states as $^2\Pi$ (π) states. The states D and M fit well with the npσ series, and we assign them as $^2\Sigma^+$ (σ) states. The states F, H′ and H fit reasonably well with the ndσ and ndπ series, but there are three states to assign and only two dipole allowed transitions to assign them to. We suspect that one of these states is the dipole forbidden ndδ transition. Because these states are so close together, we cannot decide which is which on the basis of our approximate calculations.

The α series converging to the second ionization limit of nitric oxide fits reasonably well with our nsσ series. We then assign these states as Σ^+ (σ) states.

The β and γ series converging to the third and fourth ionization limits respectively could conceivably be fit by either the npσ or npπ series, or possibly both. If we use the original data of Tanaka[4] the npσ assignment looks most likely. Hence we assign these series as npσ series. This means that the γ series

consists of $^2\Pi$ (σ) states. It does not fix the state symmetry of the β series because the symmetry of the ion core is unknown for this series.

We can compare our calculations with Hartree-Fock calculations for the states converging to the first ionization limit of nitric oxide. These calculations have been performed by Lefebre-Brion and Moser.[5] In the table below we tabulate the results of both calculations:

State	Symmetry	Lefebre-Brion, Moser		Betts, McKoy	Exp
A	$^2\Sigma^+$	3.64	3.51	3.88	3.79
E	$^2\Sigma^+$	1.51	1.62	1.64	1.72
S	$^2\Sigma^+$			.89	.95
C	$^2\Pi$	2.63		2.65	2.78
K	$^2\Pi$	1.20		1.28	1.30
D	$^2\Sigma^+$	2.53	2.47	2.62	2.66
M	$^2\Sigma^+$	1.16	1.13	1.24	1.25
F	$^2\Delta$	1.53			1.58
H′	$^2\Pi$	1.46		1.58	1.49
H	$^2\Sigma^+$	1.43		1.31	1.50

The agreement between the two calculations and experiment is in all cases very good.

The electron impact spectrum of nitric oxide has been reported by Lassettre, et al.[6] Their spectrum together with assignments is reproduced in Figure 1. In this spectrum the Rydberg states converging to the first ionization limit of nitric oxide stand out quite clearly. This spectrum does not, however, show us any new states that we did not already know about from the optical spectrum.

References

1. H. Brion, C. Moser, M. Yamazaki, J. Chem. Phys. 30, 673 (1959).
2. A. Lagerquist and E. Miescher, Can. J. Phys. 40, 352 (1962).
3. K. Huber, Helv. Phys. Acta 34, 929 (1961).
4. Y. Tanaka, Sci. Pap. I.P.C.R. 39, 456 (1942).
5. H. Lefebre-Brion, C. M. Moser, J. Mol. Spectrosc. 15, 211 (1965).
6. E. N. Lassettre, A. Skerbele, M. A. Dillon, and K. J. Ross, J. Chem. Phys. 48, 5066 (1968).

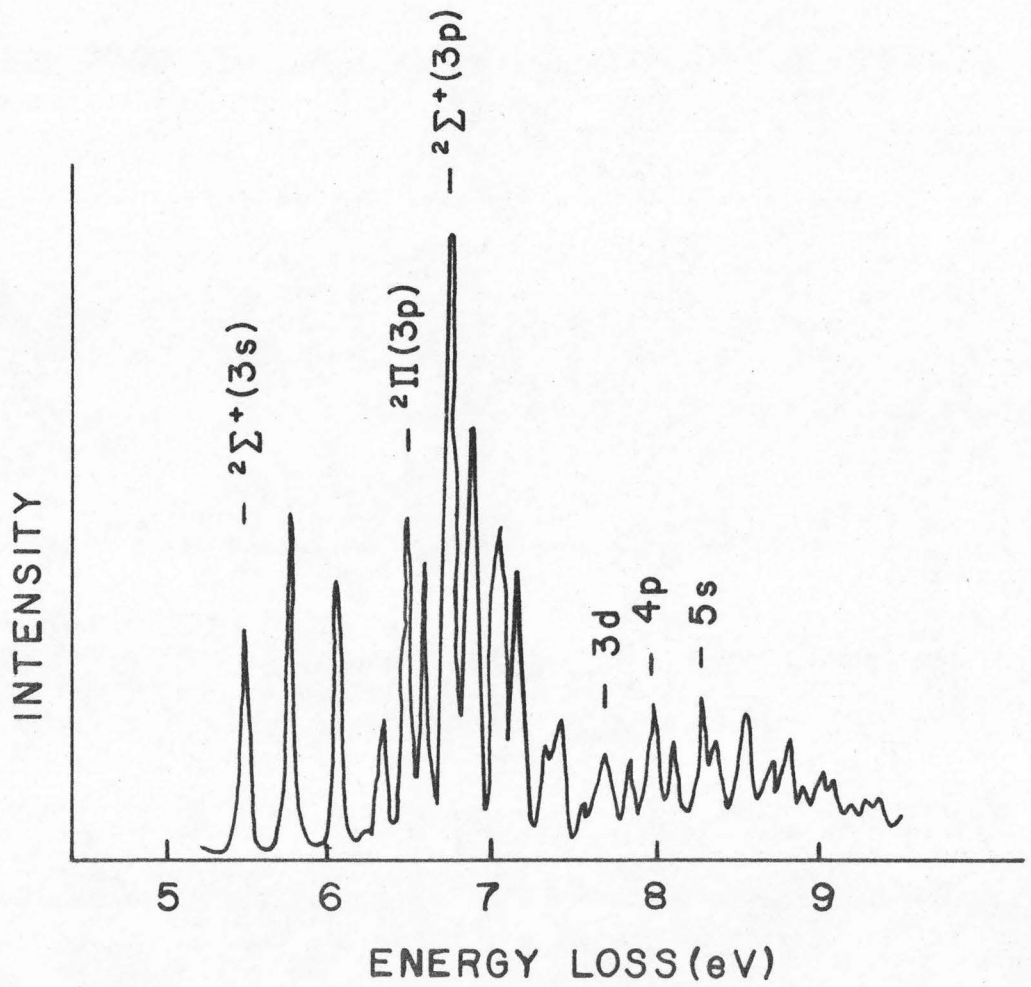


Figure 1. Electron Impact Spectrum of Nitric Oxide

4.4 CARBON MONOXIDE

Carbon monoxide is a heteronuclear diatomic belonging to the group $C_{\infty v}$. The selection rules for dipole allowed transitions from the ground state are:

$$^1\Sigma^+ \leftarrow \tilde{X} \qquad z \text{ transition}$$

$$^1\Pi \leftarrow \tilde{X} \qquad x, y \text{ transition}$$

The internuclear distance has been determined to be 2.132 a.u. for the ground state $\tilde{X}$.

Orbital energies for carbon monoxide have been calculated by many investigators. The results of Huo[1] are tabulated below:

	Minimum Basis	Extended Basis
1σ	-20.66794	-20.66123
2σ	-11.28564	-11.35927
3σ	-1.48115	-1.51920
4σ	-0.72785	-0.80235
5σ	-0.48416	-0.55304
1π	-0.55824	-0.63771
E_T	-112.3910	-112.7860

Thus we see that the electronic configuration of the ground state[2] is:

$$\{\text{core}\}(4\sigma)^2(1\pi)^4(5\sigma)^2 \; - \; ^1\Sigma^+$$

where {core} represents the orbitals:

$$(1\sigma)^1(2\sigma)^2(3\sigma)^2.$$

The electronic configuration of the Rydberg states converging to the first ionization limit of carbon monoxide will be then:

$$\{\text{core}\}\,(4\sigma)^2(1\pi)^4(5\sigma)(\text{nR})$$

and the dipole allowed transitions will be $^1\Sigma^+$ (σ) and $^1\Pi$ (π), where the symmetry in parentheses is the symmetry of the Rydberg orbital.

The electronic configuration of the Rydberg states converging to the second ionization limit of carbon monoxide will be:

$$\{\text{core}\}\,(4\sigma)^2(1\pi)^3(5\sigma)^2(\text{nR})$$

and the dipole allowed transitions will be $^1\Sigma^+$ (π) and $^1\Pi$ (σ).

Finally the electronic configuration of the Rydberg states converging to the third ionization limit of carbon monoxide will be:

$$\{\text{core}\}\,(4\sigma)(1\pi)^4(5\sigma)^2(\text{nR})$$

and the dipole allowed transitions will be $^1\Sigma^+$ (σ) and $^1\Pi$ (π).

Unlike nitrogen and oxygen the carbon monoxide optical spectrum displays several states which can be fitted into a Rydberg series converging to the first ionization limit of the ion. As given by Tanaka, Jursa and LeBlanc[3] these states are:

B	$^1\Sigma^+$	3.224
b	$^3\Sigma^+$	3.608
F	$^1\Pi$	1.637
C	$^1\Sigma^+$	2.604
c	$^3\Sigma^+$	2.586
E	$^1\Sigma^+$	2.480

In the above, the symmetry of each state is assigned on the basis of spectroscopy and does not necessarily agree with our assignments. The term values have been subtracted from the experimental ionization limit of 14.001 eV in the third column.

Furthermore, Takamine, Tanaka and Iwata[4] have observed the higher members of a Rydberg series converging to this same ion. It is:

$$113029 - R/(n - .88)^2$$

n	I.P. - ν
(5)	.799
(6)	.518
	I.P. = 14.00 eV

Tanaka[5] has observed a Rydberg series converging to the second ionization limit of carbon monoxide. He calls this series α. It has the formula:

$13380 - R/(n - .70)^2$

n	I.P. - ν
(4)	1.245
(5)	.737
(6)	.489

I.P. = 16.53 eV

Tanaka[5] has also observed two other series, which he calls β, converging to the third ionization limit of carbon monoxide. One of these series is observed to be sharp, the other is diffuse. Ogawa[6] has added two more series in addition to these β series. He calls these series III and IV. The formulae for these series are:

β (sharp)

$158680 - R/(n - .68)^2$

n	I.P. - ν
(4)	1.235
(5)	.727
(6)	.480

I.P. = 19.67 eV

β (diffuse)

$158680 - R/(n - .68)^2$

n	I.P. - ν
(4)	1.189
(5)	.700
(6)	.463

I.P. = 19.67 eV

III		IV	
$158670 - R/(n - .96)^2$		$158670 - R/(n - .20)^2$	
n	I.P. - ν	n	I.P. - ν
(4)	1.471	(3)	1.729
(5)	.824	(4)	.943
(6)	.530	(5)	.591
I.P. = 19.67 eV		I.P. = 19.67 eV	

The results of model calculations on carbon monoxide are as follows:

$ns\sigma$, δ = 1.08	$np\sigma$, δ = .72	$nd\sigma$, δ = .61
3.68	2.55	2.38
1.57	1.21	1.17
.86	.71	.65
.52	.45	

$np\pi$, δ = .74	$nd\pi$, δ = .07
2.59	1.58
1.26	1.03
.73	.55
.46	

The basis sets used were as follows. Gaussian basis functions were placed at the atomic centers, at the midpoint of the molecule and at centers 3.0 a.u. to either side of the atomic

centers on the molecular axis. For the nsσ and npσ orbitals these functions were:

Center	Exponent	Type
Carbon }	.45	s and p_z
Oxygen }	.15	
Midpoint	.05	s and p_z
	.0166	
	.0055	
	.0018	
	.0006	

For the npπ and ndπ orbitals the functions were:

Center	Exponent	Type
Carbon }	.15	p_x
Oxygen }	.05	
	.0166	
Extended Centers	.0055	p_x
	.0018	
	.0006	

Finally for the ndσ orbitals they were:

Center	Exponent	Type
Carbon } Oxygen }	.45	p_z
	.15	
	.05	
Extended Centers	.0166	p_z
	.0055	
	.0018	
	.0006	

The interpretation of the optical spectrum of carbon monoxide is fairly easy. We see that the states B and F and the Takamine, Tanaka and Iwata[4] Rydberg series all seem to be part of an nsσ Rydberg series converging to the lowest ionization limit of carbon monoxide. For this to be true the state F must be reassigned from $^1\Pi$ to $^1\Sigma^+$. That this assignment is the correct one has been confirmed recently[7, 8] both experimentally and by calculation. All of these states are then $^1\Sigma^+$ (σ_g) states.

Likewise we recognize the C $^1\Sigma^+$ state as the first member of a pσ series converging to the first ionization limit. If this is the case, then the E state cannot be a $^1\Sigma^+$ state also, and we reassign this state as the first member of a pπ series and hence $^1\Pi$ (π). This is also in agreement with reference 8.

Tanaka's α series converging to the second ionization limit of carbon monoxide fits very well with an npσ or npπ series. We cannot really distinguish which series is correct, the accuracy of our method being what it is. Therefore we simply assign this series as $^1\Sigma^+$ (π) or $^1\Pi$ (σ).

Similarly Tanaka's β series fit well with both the npσ and npπ series, and we assign these series as $^1\Sigma^+$ (σ) and $^1\Pi$ (π) without specifying which series is which.

This leaves us with the III and IV series of Ogawa to assign. Series IV fits reasonably well with our ndπ series, and we assign these states as $^1\Pi$ (π). Likewise, series III fits well with an nsσ series, despite the fact that the n = 3 member is missing. We therefore assign this series as $^1\Sigma^+$ (σ). This completes the assignments of all of the Rydberg states and series for carbon monoxide.

The results presented here are supported by the extensive Configuration Interaction calculation of reference 7. In the table below, we compare our results with those of Lefebvre-Brion, Moser and Nesbet:

	$^1\Sigma^+$	$^3\Sigma^+$	Betts, McKoy
3s	3.0	3.7	3.7
4s	1.4	1.6	1.6
3pσ	2.5	2.6	2.6
4pσ	1.2	1.2	1.2
4dσ	1.5	1.5	2.4

It is seen that the agreement between the two calculations is excellent with the single exception of the 4dσ level. We might add that our calculations were done with only a fraction of the time and expense required for these more extensive calculations.

It remains for us to compare our assignments with those of Lindholm.[9] On those states which converge to the first ionization limit we agree with Lindholm's assignments; except that he assigns the F state as $^1\Pi$, interpreting it as a $nd\pi$ state, where we would consider it to be the second member of an $ns\sigma$ series.

Likewise we agree with Lindholm on the assignment of the Tanaka α and β series, and also Ogawa's III series. Lindholm assigns the IV Ogawa series as $nd\sigma$ however, and our calculations suggest that it is $nd\pi$. Other than this Lindholm assigns two series converging to the second ionization limit of carbon monoxide, which we have not considered as well enough established to assign.

References

1. W. M. Huo, J. Chem. Phys. 43, 624 (1965).
2. G. Herzberg, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules (D. Van Nostrand Co., Inc., Princeton, New Jersey, 1967), p. 343.
3. Y. Tanaka, A. S. Jursa, and F. LeBlanc, J. Chem. Phys. 26, 862 (1957).
4. T. Takamine, Y. Tanaka and M. Iwata, Sci. Pap. I.P.C.R. (Tokyo) 40, 371 (1943).
5. Y. Tanaka, Sci. Pap. I.P.C.R. 39, 447 (1942).
6. M. Ogawa, J. Chem. Phys. 43, 2142 (1965).
7. H. LeFebvre Brion, C. M. Moser, R. K. Nesbet, J. Mol. Spectrosc. 13, 418 (1964).
8. S. G. Tilford, J. T. Vanderslice, P. G. Wilkinson, Can. J. Phys. 43, 450 (1965).
9. E. Lindholm, Arkiv. För Fysik 40, 103 (1969).

4.5 CARBON DIOXIDE

The ground state of carbon dioxide $\tilde{X}(^1\Sigma_g^+)$ is linear ($D_{\infty h}$), and the same is true for its Rydberg states. Thus, the dipole allowed transitions from the ground state are:

$^1\Sigma_u^+ \leftarrow \tilde{X}$ z transition

$^1\Pi_u \leftarrow \tilde{X}$ x, y transition

Infrared and Raman spectroscopy give a C=O bond length of 2.190 a.u. for the ground state.[1]

The orbital energies for carbon dioxide in the ground state have been calculated by McLean[2] and by Peyerimhoff, Buenker, and Whitten.[3] The results can be seen in a table from the latter author's paper:

	Peyerimhoff et al[a]		McLean[b]
$1\sigma_u$	-20.7508	-20.6621	-20.6743
$1\sigma_g$	-20.7508	-20.6620	-20.6742
$2\sigma_g$	-11.8092	-11.5322	-11.5074
$3\sigma_g$	- 1.6280	- 1.5689	- 1.5025
$2\sigma_u$	- 1.5639	- 1.5075	- 1.4632
$4\sigma_g$	- 0.8361	- 0.7867	- 0.7366
$1\pi_u$	- 0.7927	- 0.7398	- 0.6946 ($3\sigma_u$)
$3\sigma_u$	- 0.7580	- 0.7172	- 0.6792 ($1\pi_u$)
$1\pi_g$	- 0.5856	- 0.5389	- 0.4405

E_T	187.2683	-187.4929	-187.0763

[a] C=O length 2.196 a.u.

[b] C=O length 2.1944 a.u.

It is evident that there is disagreement with the order of the $3\sigma_u$ and $1\pi_u$ orbitals. This seems to be a persistent difficulty with carbon dioxide calculations. In fact, for some different basis sets, McLean gets the same ordering as Peyerimhoff, Buenker and Whitten. This fact notwithstanding, the correct ordering deduced from the series limits of the various Rydberg series is according to Herzberg[4]:

$$\{\text{core}\}\ (4\sigma_g)^2(3\sigma_u)^2(1\pi_u)^4(1\pi_g)^4 - {}^1\Sigma_g^+$$

where {core} includes the orbitals:

$$(1\sigma_u)^2(1\sigma_g)^2(2\sigma_g)^2(3\sigma_g)^2(2\sigma_u)^2$$

In the case of carbon dioxide, there are several different Rydberg states converging to several different series limits. Thus, the electronic configuration for Rydberg states converging to the ${}^2\Pi_g$ (CO_2^+) ion will be:

$$\{\text{core}\}\ (4\sigma_g)^2(3\sigma_u)^2(1\pi_u)^4(1\pi_g)^3(nR)$$

and the dipole allowed states will be ${}^1\Sigma_u^+(\Pi_u)$ and ${}^1\Pi_u(\sigma_u)$.

The electron configuration for Rydberg states converging to the $^2\Pi_u(CO_2^+)$ ion will be:

$$\{core\}\ (4\sigma_g)^2(3\sigma_u)^2(1\pi_u)^3(1\pi_g)^4(nR)$$

and the dipole allowed states will be $^1\Sigma_u^+(\pi_g)$, and $^1\Pi_u(\sigma_g)$.

The electron configuration for Rydberg states converging to the $^2\Sigma_u^+(CO_2^+)$ ion will be:

$$\{core\}\ (4\sigma_g)^2(3\sigma_u)(1\pi_u)^4(1\pi_g)^4(nR)$$

and the dipole allowed states will be $^1\Sigma_u^+(\sigma_g)$ and $^1\Pi_u(\pi_g)$.

Finally, the electron configuration for Rydberg states converging to the $^2\Sigma_g^+(CO_2^+)$ ion will be:

$$\{core\}\ (4\sigma_g)(3\sigma_u)^2(1\pi_u)^4(1\pi_g)^2(nR)$$

and the dipole allowed states will be $^1\Sigma_u^+(\sigma_u)$ and $^1\Pi_u(\pi_u)$. In all of the above cases the symmetry in paranthesis is the symmetry of the Rydberg orbital.

The optical spectrum of CO_2 begins at about 2100 Å. The region from 1750 Å to 1150 Å corresponds to transitions to two bent excited states $\tilde{A}(\{core\}(4\sigma_g)^2(3\sigma_u)^2(1\pi_u)^4(a_1)^2(b_2)(a_1)) \leftarrow \tilde{X}$ and $B(\{core\}(4\sigma_g)^2(3\sigma_u)^2(b_1)^2(a_1)(a_2)^2(b_2)^2(a_1)) \leftarrow \tilde{X}$ with maximum absorptions at about 1475 Å and 1330 Å respectively.

Below 1150 Å we find mostly Rydberg states,[5] although there still remain several unassigned progressions in this region.

There are four Rydberg series converging to the first ionization limit of carbon dioxide. The two strong series of this group are:

$111240 - R/(n - .65)^2$			$111060 - R(n - .65)^2$		
n		I.P. - ν	n		I.P. - ν
(3)	$\tilde{D}$	2.815	(3)	$\tilde{D}$	2.793
(4)	$\tilde{H}$	1.323	(4)	$\tilde{H}$	1.254
(5)	$\tilde{I}$	.766	(5)		.754
(6)		.507	(6)		.506
I.P. = 13.787			I.P. = 13.765		

and the two weak series of the group are:

$111250 - R/(n - .97)^2$			$111250 - R/(n - .57)^2$		
n		I.P. - ν	n		I.P. - ν
			(3)	$\tilde{E}$	2.407
(4)	$\tilde{G}$	1.477	(4)		1.156
(5)		.829	(5)		.687
(6)		.529	(6)		.457
I.P. = 13.789			I.P. = 13.789		

According to Herzberg[6] the two strong Rydberg series with slightly different limits (111060 and 111240 cm^{-1}) correspond to the two components of the $^2\Pi_g$ ground state of CO_2^+. Measurements on the CO_2^+ spectrum give this splitting as 160 cm^{-1}.

There are two Rydberg series converging to the second ionization limit of carbon dioxide:

$139726 - R/(n - .063 - .0069/n)^2$			$139634 - R/(n - .044 - .34/n)^2$		
n		I.P. - ν	n		I.P. - ν
(3)	$\tilde{L}$	1.570	(3)	$\tilde{M}$	1.511

(4)	.880	(4)	.886
(5)	.562	(5)	.566
I.P. = 17.319		I. P. = 17.307	

Actually there are sixteen observed series converging to this ionization potential, corresponding to transitions to different vibrational levels of the Rydberg states. Those listed above correspond to the $\nu = 0$ level, and do not include all of the members of higher n which have been observed.

The splitting of these two series, approximately 90 cm^{-1}, corresponds nicely with the splitting of the two components of the $^2\Pi_u(CO_2^+)$ ion.

There are two Rydberg series converging to the third ionization limit of carbon dioxide, known as Henning's sharp series and Henning's diffuse series respectively.

sharp series		diffuse series	
$145860 - -R/(n - .01)^2$		$145780 - R/(n - .34)^2$	
n	I.P. - ν	n	I.P. - ν
(3) $\tilde{S}$	1.607	(3) $\tilde{R}$	1.909
(4)	.803	(4)	1.002
(5)	.548	(5)	.622
(6)	.385	(6)	.420
I. P. = 18.079		I.P. = 18.069	

The identification of the lowest members of both these series is a difficult task. Tanaka, Jursa and Le Blank assigned the $\tilde{R}$ member to the $\delta = .34$ series on the basis of its diffuse appearance, but another assignment is possible and will be discussed when we interpret these results on the basis of our model calculations.

Finally, three Rydberg series have been observed by Tanaka, Jursa and Le Blank converging to the fourth ionization limit of carbon dioxide. Two are absorption series and the third appears to be an emission series.

$156350-R/(n-.71)^2$		$156410-R/(n-.56)^2$		$156400-R/(n-.05)^2$	
n	I.P. $-\nu$	n	I.P. $-\nu$	n	I.P. $-\nu$
		(emission)		(3)	1.524
(4)	1.222	(4)	1.131	(4)	.855
(5)	.715	(5)	.676	(5)	.539
(6)	.471	(6)	.457	(6)	.385
I.P. = 19.379		I.P. = 19.386		I.P. = 19.385	

Again the first members are missing, but the intensities of these series are very weak. We notice here that the doublet character of the Rydberg states converging to the two lowest ionization limits definately establishes their symmetry as π. Hence, the ordering of the orbitals, which calculations leave in some doubt, is certain. That the order of the other orbitals is now correct, we shall be able to show when we discuss the results of our model calculations.

The results of model calculations on carbon dioxide are as

follows:

$ns\sigma_g$, $\delta = 1.00$	$nd\sigma_g$, $\delta = .55$	$nd\pi_g$, $\delta = .32$
3.393	2.272	1.906
1.502	.918	.936
.842		
.520		

$np\sigma_u$, $\delta = .66$	$np\pi_u$, $\delta = .60$
2.471	2.365
1.186	1.108
.702	.587
.451	

The basis sets used in these calculations were as follows. Gaussian functions were placed at each of the atomic centers and at extended centers 3.0 a.u. to either side of the atomic centers on the molecular axis. For the $ns\sigma_g$ and $np\sigma_u$ orbital calculations these functions were:

Center	Exponent	Type
Oxygens	.45	s and p_z
	.15	
	.05	
Carbon	.0166	s and p_z
	.0055	
	.0018	
	.0006	
	.0002	

For the $np\pi_u$ orbital calculations they were:

Center	Exponent	Type
Oxygens	.45	p_x
	.15	
	.05	
	.0166	
	.0055	
	.0018	
	.0006	
Carbon	.45	p_x
	.15	
	.05	

For the $nd\sigma_g$ orbital calculations they were:

Center	Exponent	Type
Oxygens	.45	p_z
	.15	
	.05	
	.0166	
	.0055	
	.0018	
	.0006	
Carbon	.45	p_z
	.15	
	.05	

Finally, for the ndπ orbital calculations they were:

Center	Exponent	Type
Oxygens	.45	p_x
	.15	
	.05	
	.0166	
Extended Centers	.0055	p_x
	.0018	
	.0006	
	.0002	

We begin our interpretation of the optical spectrum with the four Rydberg series converging to the first ionization limit. As was remarked before, the two strong series with quantum defect $\delta = .65$ correspond to the two components of the $^2\Pi_g$ ground state of the CO_2^+ ion. We get reasonable agreement between this series and the $np\sigma_u$ calculated series, although agreement with the $np\pi_u$ series is not out of the question. Thus we assign the two strong series of Rydberg states as $^1\Pi_u(\sigma_u)$ or $^1\Sigma_u^+(\pi_u)$ which are dipole allowed.

The two weak series converging to the first ionization limit of carbon dioxide are probably dipole forbidden. Indeed this is the case for the series with quantum defect $\delta = .97$. The only possible fit is with the calculated $ns\sigma_g$ series, and the agreement is fairly close. Thus we assign these Rydberg states as $^1\Pi_g(\sigma_g)$.

It is interesting to ask why the $n = 3$ level of this series was not observed. Tanaka, Jursa and Le Blank observed a line at 86470 cm^{-1} and 87000 cm^{-1} which they say might correspond to this member. However, its weak intensity and large deviation from its expected position dissuaded them from giving it as a definite assignment.

If we look at a point 3.4 eV below the ionization potential ($\sim$ 83,800 cm^{-1}), where our calculations predict the $n = 3$ member should lie, we see the beginning of an absorption which includes the other Rydberg series we have just been discussing. It is possible that the dipole allowed strong transitions could be obscuring the dipole forbidden $^1\Pi_g \leftarrow \tilde{X}$ transition for this member. However,

when we look at an electron impact spectrum of this region, the dipole forbidden transitions appear there with moderate intensity, and there are no peaks anywhere near where one is required for the n = 3 member.

The second weak Rydberg series in this region with quantum defect $\delta = .57$ we can associate with either the $np\sigma_u$ the $np\pi_u$ or the $nd\sigma_g$ series. Since the series is weak in intensity we associate it with the dipole forbidden $nd\sigma_g$ series rather than the other two series which are dipole allowed. These states are then $^1\Pi_g(\sigma_g)$ states also.

Next we take up the two Rydberg series converging to the second ionization limit of carbon dioxide. As in the case of the strong Rydberg series of the first ionization limit, we have two similar series converging to the two component of the CO_2^+ ion.

Since the two series have practially the same quantum defect, $\delta = .06$ vs. $\delta = .04$, we can assume that they correspond to the same Rydberg orbitals. If we renumber the states and let $\delta = 1.06$ and 1.04 we see that these states must correspond with the $ns\sigma_g$ series and can be assigned as $^1\Pi_u(\sigma_g)$.

We can ask why the first members of these $ns\sigma_g$ series at 3.4 eV were not observed. They would lie at approximately 13.9 eV above the ground state $\tilde{X}$. Looking at the electron impact spectrum, it is obvious that some unaccounted for states lie in this region of the spectrum.

When we come to the third ionization limit of carbon dioxide we have an easy time. The Rydberg series with quantum defect

δ = .01 can be renumbered so that δ = 1.01, and we recognize it as an $ns\sigma_g$ series. Thus the states corresponding to these levels we assign as $^1\Sigma_u^+(\sigma_g)$ which are dipole allowed.

In order that the other series with δ = .34 be also dipole allowed we associate it with the $nd\sigma_g$ or $nd\pi_g$ calculated series. Thus, these states are $^1\Sigma_u^+(\sigma_g)$ also. The fit with the $nd\pi_g$ series is really much better than that with the $nd\sigma_g$ series, but from our experience with these calculations, the $nd\pi$ level $\tilde{R}$ at 1.9 eV appears to be spurious. Anticipating things a bit we note that there is another CO_2^+ ion about 19.4 eV above the ground state $\tilde{X}$, and that a $3s\sigma_g$ Rydberg orbital corresponding to this ion should lie within a few tenths of a eV from where $\tilde{R}$ appears. The state $\tilde{R}$, thus, could really belong to this other CO_2^+ ion but we assign the second series as an $nd\pi_g$ series anyway.

We must then somehow account for the missing first member of the Henning sharp and possibly also the diffuse series. Tanaka, Jursa and LeBlank suggest that these members may be found in the region 915 - 930 Å where there are several unassigned bands of strong intensity.

Finally, we consider the Rydberg series converging to the fourth ionization limit of carbon dioxide. We will consider the absorption series first. The series with δ = .71 fits fairly well with the $np\sigma_u$ and $np\pi_u$ orbitals, and as is the case with the similar orbitals of the first ionization limit we can not decide between them. Thus, we assign this Rydberg series as $^1\Sigma_u^+(\sigma_u)$ or $^1\Pi_u(\pi_u)$ which are dipole allowed.

The second absorption series is described by Tanaka, Jursa and Le Blank as being much weaker than the first. If we renumber the series we can make $\delta = 1.05$ and we identify this series with the $ns\sigma_g$ orbitals. Thus we assign this series as $^1\Sigma_g^+(\sigma_g)$ which is dipole forbidden, and hence weaker in intensity than the above series.

The emission series fits fairly well with the $np\sigma_u$ and $np\pi_u$ series. Using arguments similar to those for the above absorption series we assign it as $^1\Pi_u(\pi_u)$ or $^1\Sigma_u^+(\sigma_u)$.

Again we must account for the missing first members of the above series. That the first member of the $ns\sigma_g$ series might be the $\tilde{R}$ level has already been mentioned. This is also the region where Henning's first and second progressions are observed. Several of the members of Henning's progressions have now been assigned as belonging to the two Rydberg series converging to the second ionization limit of carbon dioxide. We suggest that the first members of the series which we are considering could be likewise included or obscured by these progressions.

The electron impact spectrum of carbon dioxide has been measured by two teams of investigators.[7, 8] The spectrum given by Lassettre et al. is reproduced in figure 1 together with our assignments.

We see that the electron impact spectrum yields about the same information as the optical spectrum. We note in particular that the region near the first ionization limit seems to contain peaks in addition to those converging to this limit, and we have postulated

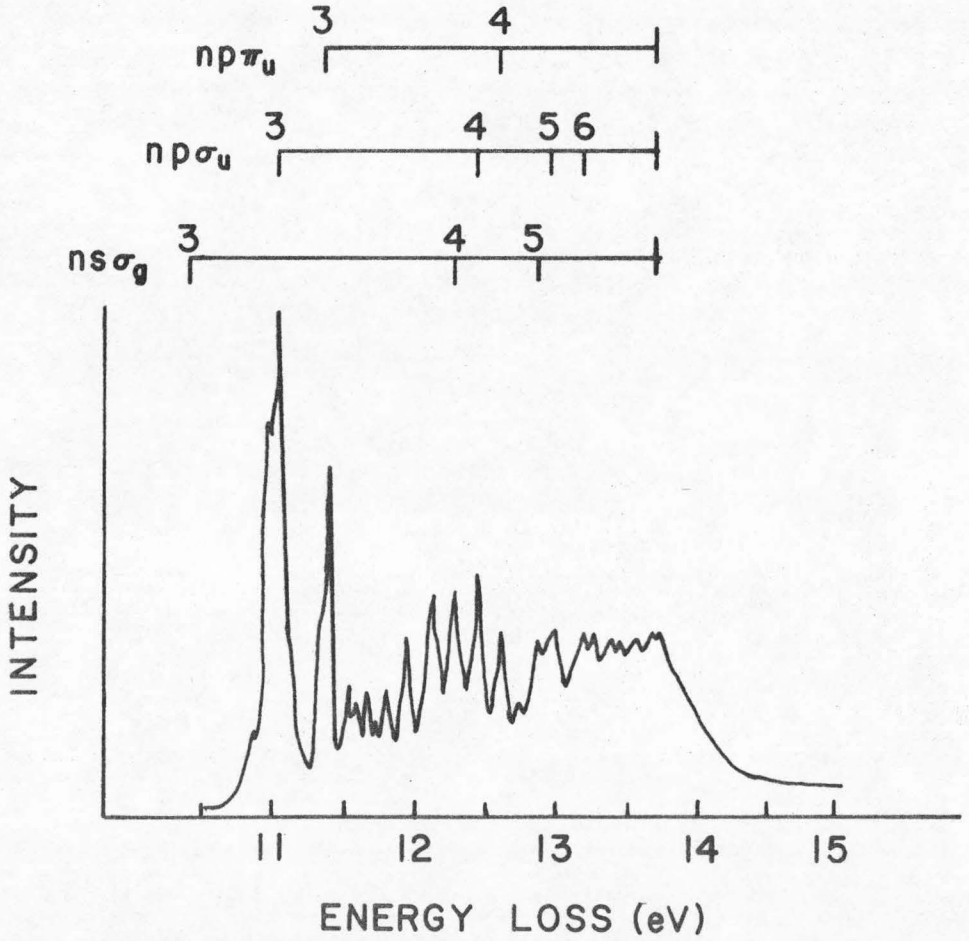


Figure 1. Electron Impact Spectrum of Carbon Dioxide

that these are the missing $3s\sigma_g$ members of the Rydberg series converging to the second ionization limit.

We run into trouble when using the electron impact spectrum when we try to find the n = 3 member of the $ns\sigma_g$ series converging to the first ionization limit. As shown on the figure 1 there appears to be no band even near the proper position. This has led Foo, Brion and Hasted to conclude that the band at 12.32 eV is the first member of the series, and hence that the quantum defect δ is zero. In spite of this we remain with our assignment inasmuch as our calculations imply that no Rydberg series of carbon dioxide can have a quantum defect of zero.

The remaining series occurring in the electron impact spectrum are fairly similar to those of the optical spectrum converging to the first ionization limit and no remarks will be made about them here. We note that in the spectrum of Foo, Brion and Hasted parts of both Henning series can be picked out in the region 16.2 - 17.2 eV.

It remains for us to compare our assignments with those of Lindholm.[9] Lindholm's assignments are made on the assumption that the quantum defects of nd series will be small or zero. This demonstrates the need for model calculations, for our results show that in the case of carbon dioxide at least, the quantum defects of the nd series are moderately large $\delta(nd\sigma_g) \simeq .55$ and $\delta(nd\pi_g) \simeq .34$. While we were not able to calculate the $nd\delta$ series we expect that the quantum defect for this series should approach that of the $nd\pi_g$ series.

Thus of the series converging to the first ionization limit we concur on the assignment of the $np\sigma_u$ series but differ with Lindholm's $np\pi_u$ and $nd\delta_g$ assignments. As to the first series, we

argue for an $nd\sigma_g$ assignment on the basis of the intensity of the optical spectrum, and because the intensity of the electron impact spectrum though strong is not that much stronger than the comparable spectrum of the other dipole-forbidden series converging to the first ionization limit. As to the latter series while we can not rule out an $nd\delta_g$ assignment we have assigned the series as $ns\sigma_g$ in spite of the difficulties raised. We agree with Lindholm that the $ns\sigma_g$ and $nd\delta_g$ assignments are the only possible ones for this series.

We agree with the assignment of the known series converging to the second ionization limit as $ns\sigma_g$; but do not consider that the other progressions cited by Lindholm have been sufficiently analyzed to warrant an assignment.

As to the Rydberg series converging to the third ionization limit; we agree with the assignment of the sharp Henning series as $ns\sigma_g$ and consider the assignment of the diffuse Henning series as a $nd\sigma_g$ as a possibility, although we would favor the assignment $nd\pi_g$. However, we cannot agree with the assignment of the peak at 16.49 eV as a $3d\pi_g$ Rydberg series member.

Finally, our objections to Lindholm's assignments of the Rydberg series converging to the fourth ionization limit are similar to our objections to his assignments for the first ionization limit. We agree with his assignment of the $np\sigma_u$ series, but consider his $np\pi_u$ series to be $nd\sigma_g$, and his $nd\pi_g$ series to be $ns\sigma_g$.

References

1. L. Pauling, The Nature of the Chemical Bond, Cornell University Press, (1960), p 267.
   D. M. Dennison, Rev. Mod. Phys. 12, 175 (1940).
2. A. D. McLean, J. Chem. Phys. 38, 1347 (1963).
3. S. D. Peyerimhoff, R. J. Buenker and J. L. Whitten, J. Chem. Phys. 46, 1707 (1967).
4. G. Herzberg, Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand, New York (1966), p. 344.
5. Y. Tanaka, A. S. Jursa, F. J. LeBlank, J. Chem. Phys. 32, 1199 (1960).
   Y. Tanaka, M. Ogawa, Can. J. Phys. 40, 879 (1962).
6. G. Herzberg, Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand, New York (1966), p. 501.
7. E. N. Lassettre, A. Skerbele, M. A. Dillon and K. J. Ross, J. Chem. Phys. 48, 5066 (1968).
8. V. Y. Foo, C. E. Brion and J. B. Hasted, Proc. Roy. Soc. (London). A322, 535 (1971).
9. E. Lindholm, Arkiv för Fysik band 40, 125 (1968).

4.6 NITROGEN DIOXIDE

The ground state of nitrogen dioxide $\tilde{X}(^2A_1)$ is bent (C_{2V}), while the NO_2^+ ions, since they are isoelectronic with carbon dioxide, are linear ($D_{\infty h}$). This means that the Rydberg states are likewise linear, making their identification a difficult job. Consequently the data for nitrogen dioxide is much less certain than for almost any other molecule that we have discussed.

From group theory we see that the dipole allowed transitions from the ground state are:

$$^2B_1 \leftarrow \tilde{X} \qquad x \text{ transition}$$

$$^2B_2 \leftarrow \tilde{X} \qquad y \text{ transition}$$

$$^2A_1 \leftarrow \tilde{X} \qquad z \text{ transition}$$

Since the upper states which we shall be interested in are linear, we rewrite these selection rules for $D_{\infty h}$ symmetry. They are:

$$^2\Pi_u \leftarrow \tilde{X} \qquad x \text{ transition}$$

$$^2\Sigma_u^+, {}^2\Pi_g \leftarrow \tilde{X} \qquad y \text{ transition}$$

$$^2\Sigma_g^+, {}^2\Pi_u \leftarrow \tilde{X} \qquad z \text{ transition}$$

Infrared and microwave spectroscopy yield the following geometrical parameters for the ground state $\tilde{X}$. We will assume

$$N{=}O \sim 2.255 \text{ a.u.} \qquad \angle ONO \sim 134.1^\circ$$

that the bond length is unchanged in the linear configuration, which is at best an approximation to the facts.

Herzberg[1] gives the electronic configuration of the ground state $\tilde{X}$ as:

$$(1b_2)^2(1a_1)^2(2a_1)^2(3a_1)^2(2b_2)^2(4a_1)^2(3b_2)^2(1b_1)^2$$

$$\times\ (5a_1)^2(1a_2)^2(4b_2)^2(6a_1)\ -\ {}^2A_1$$

The orbital energies of the lowest NO_2^+ ion have been calculated by Clementi and McLean.[2] The results they obtain are as follows:

$1\sigma_u$	- 21.3283
$1\sigma_g$	- 21.3281
$2\sigma_g$	- 16.5455
$3\sigma_g$	- 2.0957
$2\sigma_u$	- 1.9582
$4\sigma_g$	- 1.2676
$1\pi_u$	- 1.1904
$3\sigma_u$	- 1.1239
$1\pi_g$	- 0.8814
E_T	-203.1082

Thus the electronic configuration of the Rydberg states converging to the first ionization limit is expected to be:

$$\{\text{core}\}(4\sigma_g)^2(1\pi_u)^4(3\sigma_u)^2(1\pi_g)^4(nR)$$

where {core} consists of the orbitals:

$$(1\sigma_u)^2 (1\sigma_g)^2 (2\sigma_g)^2 (3\sigma_g)^2 (2\sigma_u)^2$$

Rydberg states converging to higher ionization limits are expected to have electronic configurations like:

$$\{\text{core}\} (4\sigma_g)^2 (1\pi_u)^4 (3\sigma_u)^2 (1\pi_g)^3 (5\sigma_g) (nR)$$

$$\{\text{core}\} (4\sigma_g)^2 (1\pi_u)^4 (3\sigma_u)^2 (1\pi_g)^4 (5\sigma_g) (nR)$$

$$\{\text{core}\} (4\sigma_g)^2 (1\pi_u)^3 (3\sigma_u)^2 (1\pi_g)^4 (5\sigma_g) (nR)$$

and

$$\{\text{core}\} (4\sigma_g) (1\pi_u)^4 (3\sigma_u)^2 (1\pi_g)^4 (5\sigma_g) (nR)$$

The optical spectrum of nitrogen dioxide is very extensive and has only been partially investigated. Absorption begins in the visible region (giving it an orange color) and continues weakly into the near infrared. Some of the bands in this region have been assigned to an $\tilde{A} \leftarrow \tilde{X}$ transition to a nearly linear state $\tilde{A}$ with electronic configuration:

$$(1b_2)^2(1a_1)^2(2a_1)^2(3a_1)^2(2b_2)^2(4a_1)^2(3b_2)^2(1b_1)^2$$

$$\times (5a_1)^2(1a_2)^2(4b_2)^2(2b_1) - {}^2B_1$$

At shorter wavelengths ($\sim$ 2500 Å) there is a more regular absorption leading to predissociation. This is attributed to a $\tilde{B} \leftarrow \tilde{X}$ transition, where the state $\tilde{B}$ must have symmetry $^2B_2$. A suggested possible electron configuration for this state is:

$$(1b_2)^2(1a_1)^2(2a_1)^2(3a_1)^2(2b_2)^2(4a_1)^2(3b_2)^2(1b_1)^2$$

$$\times (5a_1)^2(1a_2)^2(4b_2)(6a_1)^2 - {}^2B_2$$

A progression of bands from 2350 Å to 2000 Å may likewise be a part of the $\tilde{B} \leftarrow \tilde{X}$ system.

In the region 1650 Å to 1350 Å there is an extensive system of fairly sharp bands. This system, designated as $\tilde{E} \leftarrow \tilde{X}$, has been carefully studied by Ritchie and Walsh[3] and their conclusion is that this state is a lower member of a linear Rydberg series of symmetry $^2\Sigma_u^+$. Assuming that the series to which this state belongs converges to the lowest NO_2^+ ion, we can write the electronic configuration of the state as:

$$\{\text{core}\}(4\sigma_g)^2(1\pi_u)^4(3\sigma_u)^2(1\pi_g)^2(3p\sigma_g) \; - \; {}^2\Sigma_u^+.$$

No complete Rydberg series converging to the lowest NO_2^+ ion has been observed. Because of the difference in the geometry of the ground state $\tilde{X}$ and the linear Rydberg states, transitions to these states are expected to have an extended structure like the $\tilde{E} \leftarrow \tilde{X}$ transition, and therefore to involve a detailed analysis for their identification.

Nakayama, Kitamura and Watanabe[4] have observed a weak photoionization at 9.78 eV which they attribute to the first ionization potential. They likewise assign a break in the photoionization curve at 10.83 eV as a dissociation process:

$$NO_2 + h\nu \rightarrow NO^+ + O^-$$

The problem of identification continues to plague the investigation of Rydberg series converging to other, higher energy NO_2^+ ions. In the region 1300 Å to 1100 Å Price and Simpson[5] identified two short progressions of strong but diffuse bands starting at 1280 Å and 1135 Å respectively. Assuming that these corresponded to early members of a Rydberg series converging to a higher NO_2^+ ion, they identified a Rydberg series with the formula

$$99500 - R/(n - 0.75)^2 \qquad n = 3, 4, \ldots$$

with a corresponding ionization potential of 12.3 eV.

Nakayama, Kitamura and Watanabe fitted these small bands, and several other bands which they observed, into a Rydberg series

with the different formula:

$$93695 - R/(n - 0.79)^2 \qquad n = 4, 5, \ldots$$

with a corresponding ionization potential of 11.62 eV.

Finally Tanaka and Jursa[6] observed the above two progressions and a new progression around 1070 Å. They were able to fit this new progression onto the Price and Simpson progression by modifying the Rydberg formula slightly to:

$$97350 - R/(n - 0.65)^2 \qquad n = 3, 4, \ldots$$

with a corresponding ionization potential of 12.07 eV. Unfortunately Tanaka and Jursa could not observe the higher members of the progression and confirm absolutely the existence of this Rydberg series.

Tanaka and Jursa also cast doubt on the existence of the Nakayama, Kitamura and Watanabe series. As described by them, under high resolution, the n = 4 member of the series is a close triplet, the n = 5 member is single and diffuse, the n = 6, 7 members are doublets and the n = 8 member is single, narrow and of more intensity than the n = 6 and 7 members.

Tanaka and Jursa have also identified four Rydberg series converging to a much higher NO_2^+ ion. Three of the series are strong, and two of these may be vibrational bands of the same transition. They are:

I (strong)

$152100 - R/(n - 0.15)^2$

n		I.P. - ν
(2)	$^1\Sigma$	5.023
(3)		1.655
(4)		.904
(5)		.568

I.P. = 18.840

II (weak)

$152290 - R/(n - 0.67)^2$

n		I.P. - ν
(3)	$^3\Sigma$	2.555
(4)		1.235
(5)		.737
(6)		.479

I.P. = 18.876 eV

III (strong)

$152160 - R/(n - 1.03)^2$

n	I.P. - ν
(3)	3.483
(4)	1.587
	1.541
(5)	.892
	.859

I.P. = 18.860

IV (strong)

$152390 - R/(n - 1.03)^2$

n	I.P. - ν
(3)	3.086
(4)	1.486
	1.441
(5)	.860
	.820

I.P. = 18.888

The n = 2 member of the series I at 897.0 Å practically coincides with a strong NO band (the n = 5 member of the α series). Despite this fact, and despite the large quantum defect of this level (δ = .36), Tanaka and Jursa feel that it is really a part of the NO_2 series.

Model calculations on linear nitrogen dioxide yield the following results:

$ns\sigma_g$, $\delta = 1.05$	$np\sigma_u$, $\delta = .66$	$nd\sigma_g$, $\delta = .21$
3.092	2.495	1.746
1.566	1.199	.931
.872	.707	
.531	.452	

$np\pi_u$, $\delta = .65$	$nd\pi_g$, $\delta = 0.0$
2.466	1.509
1.165	1.049
.644	.717
.406	

The basis sets for the calculations were as follows. Gaussian functions were placed at each of the atomic centers and at centers 3.0 a.u. to either side of the atomic centers on the molecular axis. For the $ns\sigma_g$ and $np\sigma_u$ orbital calculations these functions were:

Center	Exponent	Type
Oxygens	.45	s and p_z
	.15	
	.05	
Nitrogen	.0166	s and p_z
	.0055	
	.0018	
	.0006	
	.0002	

For the $np\pi_u$ orbital calculations they were:

Center	Exponent	Type
Oxygens	.45	p_x
	.15	
	.05	
	.0166	
	.0055	
	.0018	
	.0006	
Nitrogen	.45	p_x
	.15	
	.05	

For the $nd\sigma_g$ orbital calculations they were:

Center	Exponent	Type
Oxygen	.45	p_z
	.15	
	.05	
	.0166	
	.0055	
	.0018	
	.0006	
Nitrogen	.45	p_z
	.15	
	.05	

Finally for the $nd\pi_g$ orbital calculations they were:

Center	Exponent	Type
Oxygen	.45	p_x
	.15	
	.05	
	.0166	
Extended Centers	.0055	p_x
	.0018	
	.0006	
	.0002	

The results of our calculations can be most helpful in interpreting the optical spectrum.

Our first result is the confirmation of the results of Ritchie and Walsh on the assignment of the $\tilde{E} - \tilde{X}$ transition, and the estimate of Nakayama, Kitamura and Watanabe for the first ionization limit. Assuming that the $\tilde{E}$ state (at approximately 58309 cm^{-1}) is the n = 3 member of an $np\sigma_u$ series, we would predict that the first ionization limit is at

$$7.23 + 2.50 = 9.73 \text{ eV}$$

in good agreement with the predicted 9.78 eV.

As to the proposed Rydberg series with ionization limits at 12.3, 11.62, and 12.07 eV, we can be less definite. We note that they all seem to be more or less consistent with an $np\sigma_u$ or $np\pi_u$

series. Photoelectron spectroscopy predicts ionization limits of 10.97, 12.82, 13.48, 14.01, 14.37, 16.79 and 18.86 for nitrogen dioxide.

The four series converging to the NO_2^+ ion with ionization potential at 18.86 eV are readily identified. Except for the n = 2 member the series I fits nicely with the ndσ series, and we identify the series as $^2\Sigma_g^+$ (ndσ_g). We would dispute the fact that the n = 2 member is actually a member of series I. Actually, this band lies 2.97 eV below the ionization limit found by photoelectron spectroscopy at 16.79 eV. Thus it could be the first member of a nsσ_g series converging to this ion. It would then be a $^2\Pi_u$ (3sσ_g) state.

The series II can be identified with either an npσ_u or npπ_u series, making its assignment either $^2\Sigma_u^+$ (σ_u) or $^2\Pi_u$ (π_u).

Lastly, we would identify the two series III and IV as vibration bands of the same nsσ_g series, making its assignment $^2\Sigma_g^+$ (nsσ_g).

The state assignments made above are made on the assumption that these Rydberg states have the electronic configuration of the 5th and last Rydberg configuration given in the early part of the discussion of nitrogen dioxide. This assignement is based upon an analogy with the carbon dioxide spectrum. According to this line of reasoning Rydberg series corresponding to the third and fourth electron configurations should have ionization limits at about 17.5 eV. Bands which would correspond to these series, in the region 720 Å to 850 Å, have been

observed by Tanaka and Jursa. However, because of their weak and confusing nature, these bands have not as yet been analyzed.

References

1. G. Herzberg, Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand, New York (1966), p. 345.
2. E. Clementi and A. D. McLean, J. Chem. Phys. 39, 323 (1963).
3. R. W. Ritchie, A. D. Walsh, Proc. Royal Soc. 267A, 395 (1962).
4. T. Nakayama, M. Y. Kitamura, K. Watanabe, J. Chem. Phys. 30, 1180 (1959).
5. W. C. Price, D. M. Simpson, Trans. Faraday Soc. 37, 106 (1941).
6. Y. Tanaka, A. S. Jursa, J. Chem. Phys. 36, 2493 (1962).

4.7 NITROUS OXIDE

The ground state of nitrous oxide $\tilde{X}(^1\Sigma^+)$ is linear ($C_{\infty v}$), and the same can be said for its Rydberg states. Thus the selection rules for dipole allowed transitions are simple.

$^1\Sigma^+ \leftarrow \tilde{X}$ z transition

$^1\Pi \leftarrow \tilde{X}$ x, y transition

being the allowed transitions from the ground state $\tilde{X}$.

Infrared and microwave spectroscopy give the following geometrical parameters for nitrous oxide

$N = N \sim 2.128$ a.u. $\qquad N = O \sim 2.251$ a.u.

The orbital energies of nitrous oxide have been calculated by Peyerimhoff and Buenker[1] and by McLean and Yoshimine.[2] Their results can be summarized by a table taken from Peyerimhoff and Buenker.

	Peyerimhoff and Buenker		McLean and Yoshimine
1σ	-20.7123	-20.6582	-20.6506
2σ	-16.1096	-15.8609	-15.8403
3σ	-15.8985	-15.7429	-15.6947
4σ	- 1.6781	- 1.6441	- 1.6105
5σ	- 1.5110	- 1.4678	- 1.4240
6σ	- 0.8584	- 0.8218	- 0.8317

1π	- 0.8412	- 0.7823	- 0.7618
7σ	- 0.7373	- 0.6977	- 0.6987
2π	- 0.5314	- 0.4875	- 0.4914
E_T	-183.3404	-183.5763	-183.7567

The electron configuration for the ground state $\tilde{X}$ is then:

$$\{\text{core}\}(6\sigma)^2(1\pi)^4(7\sigma)^2(2\pi)^4 - {}^1\Sigma^+$$

where $\{\text{core}\}$ denotes the orbitals:

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2$$

The electronic configuration of the Rydberg series converging to the first ionization limit is:

$$\{\text{core}\}\ (6\sigma)^2(1\pi)^4(7\sigma)^2(2\pi)^3(\text{nR})$$

and the dipole allowed Rydberg transitions will be ${}^1\Sigma^+(\pi)$ and ${}^1\Pi(\sigma)$, where the symmetry in parenthesis is the symmetry of the Rydberg orbital.

Similarly, the electronic configuration of the Rydberg series converging to the second ionization limit will be:

$$\{\text{core}\}\ (6\sigma)^2(1\pi)^4(7\sigma)(2\pi)^4(\text{nR})$$

and the dipole allowed transitions will be ${}^1\Sigma^+(\sigma)$ and ${}^1\Pi(\pi)$.

The electronic configuration of the Rydberg series converging to the third ionization limit will be

$$\{\text{core}\}(6\sigma)^2(1\pi)^3(7\sigma)^2(2\pi)^4(nR)$$

and the dipole allowed transitions will be $^1\Sigma^+(\pi)$ and $^1\Pi(\sigma)$.

Finally the electronic configuration of the Rydberg series converging to the fourth ionization limit will be:

$$\{\text{core}\}(6\sigma)(1\pi)^4(7\sigma)^2(2\pi)^4(nR)$$

and the dipole allowed transitions will be $^1\Sigma^+(\sigma)$ and $^1\Pi(\pi)$.

Nitrous oxide begins to absorb in the near ultraviolet. The spectrum starts with three continua with maxima at 2900 Å, 2730 Å and 1820 Å.

These continua have been assigned to transitions to the states $\tilde{a}$ ($\{\text{core}\}(6\sigma)^2(1\pi)^4(7\sigma)^2(2\pi)^3(3\pi)$-$^3\Pi$), $\tilde{b}$($\{\text{core}\}(6\sigma)^2(1\pi)^4(7\sigma)^2(2\pi)^3(3\pi)$-$^3\Pi$), and $\tilde{A}$($\{\text{core}\}(6\sigma)^2(1\pi)^4(7\sigma)^2(2\pi)^3(3\pi)$ - $^1\Sigma^+$). A discrete absorption between 1600 Å and 1400 Å has been assigned to a transition to a bent excited state $\tilde{B}$ ($\{\text{core}\}(6\sigma)^2(1\pi)^4(7\sigma)^2(2\pi)^2(3\pi)^2$-$^1\Pi$).

The next feature to appear in the spectrum is another continuum between 1350 Å and 1230 Å, assigned to the transition $\tilde{C}$ ($\{\text{core}\}(6\sigma)^2(1\pi)^4(7\sigma)^2(2\pi)^3(8\sigma)$ -$^3\Pi$?) ← $\tilde{X}$. Near the maximum of this continuum at 1292 Å, there is a single sharp peak. According to Herzberg[3] "it is not clear whether the continuum or the peak is the first member of a Rydberg series."

Beyond this region we have two Rydberg series converging to the $^2\Pi$ ion of N_2O^+. As observed by Tanaka, Jursa and LeBlank, [4] these are:

I		II	
$104000 - R/(n-.60)^2$		$104300 - R/(n-.68)^2$	
n	I.P.$-\nu$	n	I.P. $-\nu$
(3)	2.400	(3)	2.398
(4)	1.146	(4)	1.164
(5)	.687	(5)	.706
(6)	.474	(6)	.489
I.P. = 12.890 eV		I.P. = 12.928 eV	

As measured from the N_2O^+ spectrum the splitting of the components of this ion should be approximately 133 cm^{-1} instead of 300 cm^{-1}. The poor agreement is blamed on the fact that the second Rydberg series could not be followed in its higher members.

A few irregular bands occur around the n = 3 members of the above series, [5] what they correspond to is not understood as yet.

Two further Rydberg series are observed to converge to the $^2\Sigma^+$ N_2O^+ ion. The assignment of this ion is confirmed by the difference of its ionization limit from that of the lowest N_2O^+ ion. This difference of 28230 cm^{-1} (3.499 eV) compares remarkably well with the measured energy of the $^2\Sigma^+$ state of N_2O^+ above the ground state (28229.8 cm^{-1}). The two series are:

III

$132210 - R/(n-1.00)^2$

n	I.P. - ν
(3)	4.028
(4)	1.557
(5)	.860
(6)	.546

I.P. = 16.387 eV

IV

$132250 - R/(n - .22)^2$

n	I.P. - ν
(3)	1.775
(4)	.958
(5)	.603

I.P. = 16.392 eV

Actually a third series V was observed converging to a limit of 133490 cm^{-1}, but this was identified as a vibrational member of the first series.

Finally, converging to the fourth highest ion of NO_2^+ we have four Rydberg series:

VI

$162130 - R/(n - .31)^2$

n	I.P. - ν
(3)	1.833
(4)	.991
(5)	.612

I.P. = 20.095 eV

VII

$162200 - R/(n - .06)^2$

n	I.P. - ν
(3)	1.562
(4)	.865
(5)	.557

I.P. = 20.104 eV

VIII

$162200 - R/(n-.68)^2$

n	I.P. - ν
(3)	2.556

IX

$162160 - R/(n-.58)^2$

n	I.P. - ν
(3)	2.387

(4)	1.238	(4)	1.146
(5)	.731	(5)	.684
(6)	.486	(6)	.460
I.P. = 20.104 eV		I.P. = 20.099 eV	

Model calculations on nitrous oxide yield the following results:

$ns\sigma$, δ = 1.04	$np\sigma$, δ = .65	$nd\sigma$, δ = .80
3.554	2.459	2.813
1.575	1.186	1.484
.873	.702	.643
.531	.451	

$np\pi$, δ = .68	$nd\pi$, δ = .24
2.538	1.576
1.238	1.064
.746	.648
.471	

The basis sets for the calculations were as follows: Gaussian functions were placed at each of the atomic centers and at centers 3.0 a.u. from the ends of the molecule on the molecular axis. For the $ns\sigma$ and $np\sigma$ orbital calculations these functions were:

Center	Exponent	Type
Oxygen	.45	s and p_z
Outer Nitrogen	.15	

	.05	
Inner Nitrogen	.0166	s and p_z
	.0055	
	.0018	
	.0006	
	.0002	

For the npπ orbital calculations they were:

Center	Exponent	Type
Oxygen	.45	p_x
Outer Nitrogen	.15	
	.05	
	.0166	
	.0055	
	.0018	
	.0006	
Inner Nitrogen	.45	p_x
	.15	
	.05	

For the ndσ orbital calculations they were:

Center	Exponent	Type
Oxygen	.45	p_z
Outer Nitrogen	.15	
	.05	
	.0166	
	.0055	
	.0006	

Inner Nitrogen	.45	p_z
	.15	
	.05	

Finally for the ndπ orbital calculations, they were

Center	Exponent	Type
Oxygen	.45	p_x
Outer Nitrogen	.15	
	.05	
	.0166	
Exterior Centers	.0055	p_x
	.0018	
	.0006	
	.0002	

The interpretation of the optical spectrum based upon the model calculations goes as follows.

The two series converging to the $^2\Pi$ N_2O^+ ion correspond to one set of orbitals converging to the two components of the ion. The best fit for these orbitals is with the npσ series, although the npπ is not out of the question. We assign these Rydberg states as $^1\Pi(np\sigma)$ or $^1\Sigma^+(np\pi)$.

The series with quantum defect 1.00 converging to the $^2\Sigma^+$ NO_2^+ ion we can identify with the nsσ series. We therefore assign these Rydberg states as $^1\Sigma^+(ns\sigma)$. The other series with quantum defect $\delta = .22$ fits reasonably with our ndπ series, and it is definitely not one of the other dipole allowed series. We assign these states as $^1\Pi(nd\pi)$.

Again, when we interpret the Rydberg Series converging to the fourth ionization limit we see that the series with quantum defect $\delta \approx .31$ fits reasonably with an $nd\pi$ series, and we assign these states as $^1\Pi(nd\pi)$. The series with quantum defect $\delta = .06$ we can renumber to get $\delta \doteq 1.06$. We see that this corresponds to our $ns\sigma$ series, so that these Rydberg states are $^1\Sigma^+(ns\sigma)$. The two series with quantum defects $\delta = .68$ and $.58$ we can correlate best with the $np\pi$ and $np\sigma$ series respectively, although the opposite assignment is not excluded. We then assign these states as $^1\Pi(np\pi)$ and $^1\Sigma^+(np\sigma)$.

We can ask what has become of the n = 3 member of the $^1\Sigma^+(ns\sigma)$ series. It should lie at approximately 133,600 cm^{-1} or slightly above the ionization limit of the series converging to the $^2\Sigma^+$ N_2O^+ ion. It may well be buried somewhere within this limit.

We note here that the Rydberg state symmetries for the last ion above assume that this ion corresponds to the $^2\Sigma^+$ N_2O^+ ion (i.e., fourth ionization limit) and not the lower lying $^2\Pi$ ion. That this is the case is supported by the work of Cook and Ching.[6]

The electron impact spectrum of nitrous oxide has been measured by both Lassettre, Skerbele, Dillon and Ross[7] and by Foo, Brion, and Hasted.[8] The spectrum of Foo, Brion and Hasted is reproduced in figure 1.

We see that the series I-VII can be identified with more or less certainty, and that for these series the electron-impact data adds very little to the optical picture which we have built up earlier.

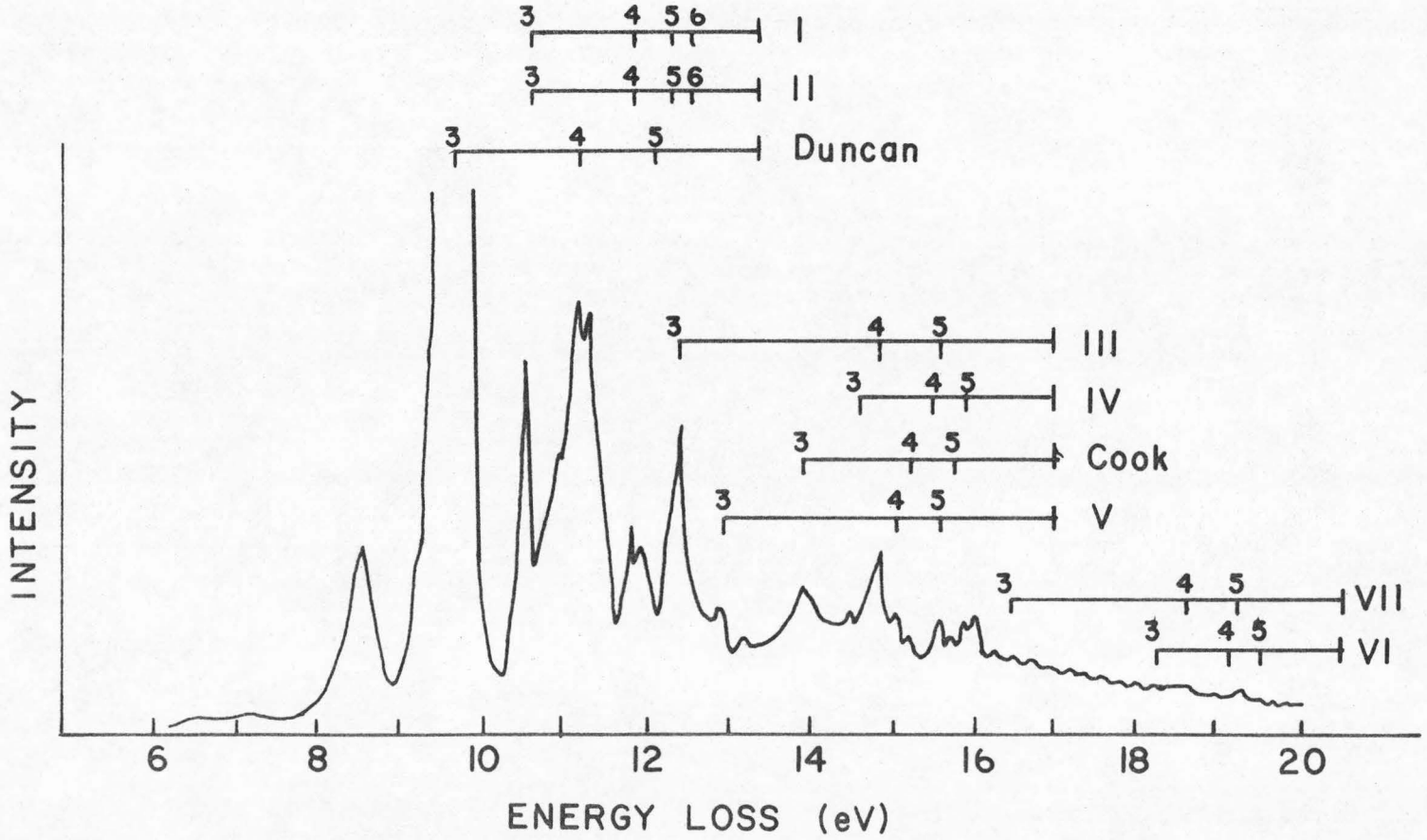


Figure 1. Energy Loss Spectrum of Nitrous Oxide

However, the series labeled Duncan is something new. This series was the first Rydberg series assigned to N_2O by Duncan[9] in 1936. Subsequently, it was re-interpreted, and it is not listed as a Rydberg series by Herzberg. Its formula according to Duncan is

$$102567 - R/(n-0.92)^2 \quad n = 3, 4...$$

with an ionization limit of 12.66 eV. The first member of this series is the sharp peak at 1292 Å which was so prominent in the optical spectrum. The original bands assigned to this series were:

n	Band	12.66 - ν
(3)	77900 cm^{-1}	3.057
(4)	91200	1.409
(5)	95852	.832
(6)	98326	.526
(7)	99609	.367
(8)	100379	.272

If we shift these bands to correspond to the correct ionization potential of 12.9 eV, we see that with the exception of the n = 5 band they fit reasonably well with an nsσ series.

n	Band	12.9 - ν
(3)	77900 cm^{-1}	3.245
(4)	91200	1.596
(5)	95852	1.019
(6)	98326	.713

(7)	99609	.554
(8)	100379	.458

Thus we assign these states, with the exception of n = 5 as $^1\Pi(ns\sigma)$ Rydberg states, re-establishing Duncan's Rydberg series.

Finally, there is a series converging to the second ionization limit at 16.39 eV reported by Cook[10] et al, whose first member at 13.9 eV is consistent with an $np\pi$ or $np\sigma$ series, and hence the states are $^1\Pi(np\pi)$ or $^1\Sigma^+(np\sigma)$. This is about the limit of information that can be gotten out of the electron-impact spectrum at present.

As in the case of carbon dioxide, we can for nitrous oxide again compare our predictions with those of Lindholm.[11] Our results agree for the Rydberg states converging to the lowest N_2O^+ ion with the exception that we do not assign any nd transitions.

Our assignments for the series converging to the second ionization limit agree, except that our calculations indicate that the $nd\sigma$ series must have an appreciable quantum defect $\delta \gg .22$, so that we assign as $nd\pi$ the series which Lindholm assigns as $nd\sigma$.

When it comes to the Rydberg series converging to the fourth ionization limit we agree with Lindholm as to the np series. However, we assign his $nd\pi$ series as $ns\sigma$ and again identify as $nd\pi$ the series he assigns a $nd\sigma$. In general then, we agree as to the assignments of the np series, differ somewhat on the ns series and quite frequently in the assignments of the various nd series.

References

1. S. D. Peyerimhoff and R. J. Buenker, J. Chem. Phys. 49, 2473 (1968).
2. A. D. McLean and M. Yoshimine, IBM J. Res. Develop. 12, 206 (1968).
3. G. Herzberg, Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand, New York (1966), p. 505.
4. Y. Tanaka, A. S. Jursa and F. J. LeBlank, J. Chem. Phys. 32, 11205 (1960).
5. M. Zelikoff, K. Watanabe, E. C. Y. Inn, J. Chem. Phys. 21, 1643 (1953).
6. G. R. Cook, B. K. Ching, Rep. T. D. R. 469 (9260-01)-4 (1969).
7. E. N. Lassettre, A. Skerbele, M. A. Dillon and K. J. Ross, J. Chem. Phys. 48, 5066 (1968).
8. V. Y. Foo, C. E. Brion and J. B. Hasted, Proc. Roy. Soc. 322 A, 535 (1971).
9. A. B. F. Duncan, J. Chem. Phys. 4, 638 (1936).
10. G. R. Cook, P. H. Metzger, M. Ogawa, J. Opt. Soc. Am. 58, 129 (1968),
    G. R. Cook, B. K. Ching, ibid.
11. E. Lindholm, Arkiv för Fysik, 40, 129 (1969).

4.8 ACETYLENE

The ground state of acetylene $\tilde{X}(^1\Sigma_g^+)$ is linear ($D_{\infty h}$), and while there is spectroscopic evidence that some excited states are bent, the Rydberg states with which we have to deal have been shown to be linear. Hence, the group theory for the molecule is straightforward:

$$^1\Sigma_u^+ \leftarrow \tilde{X} \text{ ; z transition}$$
$$^1\Pi_u \leftarrow \tilde{X} \text{ ; x, y transitions}$$

being the dipole allowed transitions.

Infrared and Raman spectroscopy yield the following bond lengths for the ground state:

C - H	1.999 a.u.
C≡C	2.282 a.u.

The orbital energies for acetylene have been calculated by several investigators. The results can best be summarized by a table taken from Buenker, Peyerimhoff, and Whitten:[1]

	Buenker et al.[a]		McLean[b]	Moskowitz[b]	Palke[a]
$1\sigma_g$	-11.4141	-11.2585	-11.3998	-11.2646	-11.2978
$1\sigma_u$	-11.4105	-11.2548	-11.3971	-11.2610	-11.2951
$2\sigma_g$	- 1.0897	- 1.0406	- 1.0414	- 1.0417	- 1.0048
$2\sigma_u$	- 0.8069	- 0.7658	- 0.7758	- 0.7588	- 0.7513
$3\sigma_g$	- 0.7309	- 0.6835	- 0.6827	- 0.6708	- 0.6563

$1\Pi_u$	- 0.4761	- 0.4131	- 0.4413	- 0.4023	- 0.4056
$1\Pi_g$	0.2058	0.1795	0.2510		0.3058
E_T	-76.7218	-76.7916	-76.5438	-76.7418	-76.6165

[a] With carbon-carbon bond distance 2.272 a.u.

[b] With carbon-carbon bond distance 2.281 a.u.

From the above we see that we can write the electron configuration for the ground state $\tilde{X}$ as:

$$\{\text{core}\}\ (1\pi_u)^4 - {}^1\Sigma_g^+$$

where {core} consists of the orbitals:

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2.$$

Similarly, we can write the electronic configuration of the Rydberg states as:

$$\{\text{core}\}\ (1\pi_u)^3(nR)$$

In order that transitions between the ground and Rydberg state be dipole allowed, the latter must be either ${}^1\Sigma_u^+$ (π_g) or ${}^1\pi_u$ (σ_g). The symmetry notation included between parenthesis being the symmetry of the Rydberg orbital.

Turning to the optical spectrum we find the following. The long wavelength region from 2400 Å to 2100 Å consists of progressions belonging to the bent excited state

$$A(\{\text{core}\}(1\pi_u)^3(1\pi_g)) \leftarrow \tilde{X}.$$

From 2000 Å to 1550 Å there are a series of diffuse bands which as yet have not been sufficiently well analyzed to be identified with certainty.

When we reach shorter wavelengths (1550 Å to 1100 Å) we meet with strong transitions which can be fitted into two distinct Rydberg series.

R			R′		
$91950 - R/(n-.95)^2$			$92076 - R/(n-.50)^2$		
n		I.P. - ν	n		I.P. - ν
(3)	$\tilde{C}$	3.243	(3)	$\tilde{D}$	2.176
(4)		1.467	(4)		1.107
(5)		.834	(5)		.670
(6)		.535	(6)		.451
I.P. = 11.397			I.P. = 11.412		

The facts that the O—O vibrational transition is the strongest transition observed in each band, and that only totally symmetric C—C vibrations are excited confirm that these are linear Rydberg states.

Herzberg[2] has studied the 2nd member of the R series (at 1250 Å) at high resolution and finds its symmetry to be $^1\Pi_u$.

Furthermore, Price[3] has noted that the two series have different rotational substructures. The R series possesses P, Q, and

R branches; and the R′ only P and R branches. This would imply a symmetry of $^1\Sigma_u^+$ for the members of the R′ series.

In addition to the two Rydberg series identified above, Wilkinson[4] has identified two bent excited states in the region 1550 Å - 1100 Å. He calls these states B and C, in Herzberg's notation they are $\tilde{E}$ and $\tilde{F}$. In addition to these, Nakayama and Watanabe have added a third bent excited state, which they call D[5]. All of these transitions can be seen on an intensity plot taken from Nakayama and Watanabe (Fig. 1).

The results of model calculations on acetylene are as follows:

$ns\sigma_g$, $\delta = .99$	$nd\sigma_g$, $\delta = .59$	$nd\pi_g$, $\delta = .33$
3.441	2.345	1.543
1.496	1.152	1.014
.836	.709	.538
.513	.473	

$np\sigma_u$, $\delta = .64$	$np\pi_u$, $\delta = .68$
2.453	2.522
1.179	1.225
.679	.761
.447	.464

The basis sets used in these calculations were as follows: The two hydrogen atoms were neglected, reducing the problem to a diatomic C≡C with D_{∞_h} symmetry. Gaussian functions were put at centers located on the atomic centers themselves, at the midpoint

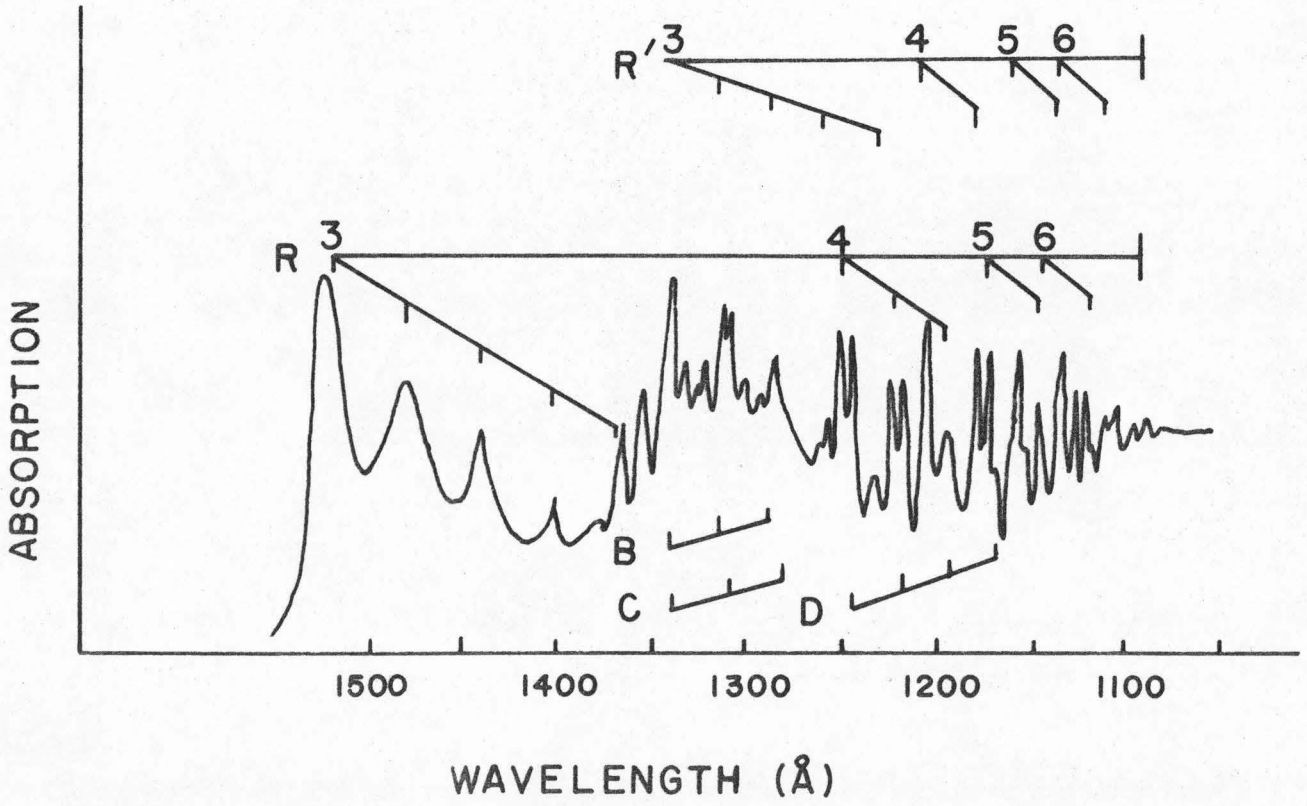


Figure 1. Absorption Coefficients of Acetylene

of the molecule and at centers 3.0 a.u. outside of the atomic centers on the molecular axis. For the $ns\sigma_g$ and $np\sigma_u$ orbital calculations these functions were:

Center	Exponent	Type
Carbons	.45	s and p_z
	.15	
Midpoint	.05	s and p_z
	.0166	
	.0055	
	.0018	
	.0006	

For the $np\pi_u$ orbital calculations they were

Center	Exponent	Type
Carbons	.15	p_x
	.05	
	.0166	
	.0055	
Midpoint	.0018	p_x
	.0006	
	.0002	

For the $nd\sigma_g$ orbital calculations they were:

Center	Exponent	Type
Carbons	.45	p_z

	.15	
	.05	
Outside	.0166	p_z
Centers	.0055	
	.0018	
	.0006	
	.0002	

Finally, for the $nd\pi_g$ orbitals these functions were:

Center	Exponent	Type
Carbons	.15	p_x
	.05	
	.0166	
Outside	.0055	p_x
Centers	.0018	
	.0006	

Comparing the results of the model calculations with the experimental data we see that the R series and the ns σ_g orbitals correlate very nicely. The R′ series could be fit with either nd σ_g or the $nd\pi_g$ orbitals. The spectroscopic data on the rotational substructure decides in favor of the $nd\pi_g$ assignment, but we suspect that some $^1\Pi_u$ (nd σ_g) states must lie close by, at slightly larger wavelengths. In fact, as can be seen on the Nakayama and Watanabe intensity plot there is an unassigned transition of fairly strong intensity near the 3R′ band which might be the first member

of such a series.

The electron impact spectrum of acetylene has been studied at high resolution by Lassettre[6] and coworkers. Their spectrum together with our assignments are given in figure 2.

We see that the electron impact spectrum is fairly similar to the optical spectrum. Again we have a state which we can assign as $^1\Pi_u(3d\sigma_g)$ at slightly lower energy than the $^1\Sigma_u^+(3d\pi_g)$ state, suggesting the existence of an $nd\sigma_g$ series with slightly larger wavelengths than the $nd\pi_g$ series.

We can compare our results with those of Greene, Barnard and Duncan.[7] These authors calculated the $ns\sigma_g$ and $nd\pi_g$ series for acetylene. For the $nd\sigma_g$ series their results compare with ours as follows:

	$ns\sigma_g$	
n	E(Duncan et al)	E(Betts, McKoy)
(3)		3.441
(4)	.0295230 (1.457)	1.496
(5)	.0295230 (.803)	.836
(6)	.0189525 (.516)	.513
(7)	.0132392	
(8)	.00977478	
(9)	.00749517	
(10)	.00582070	

For the $nd\pi_g$ series their results are:

$nd\pi_g$

n	E(Duncan et al)	E(Betts, McKoy)
(3)	.0669519 (1.822)	1.543
(4)	.0358242 (.975)	1.014
(5)	.0223257 (.608)	.538
(6)	.0151341	
(7)	.0110445	
(8)	.00836006	
(9)	.00652330	
(10)	.00348021	

Because of the difficulty and expense of evaluating the integrals involved in their calculation, Greene, Barnard and Duncan replaced the $C_2H_2^+$ core with a spherically symmetric effective core. This replacement core contained 3s functions, and hence made it impossible to calculate the n = 3 members of the $ns\sigma_g$ series. Other than this, the agreement between their $ns\sigma_g$ series and ours is very good.

The agreement between the $nd\pi_g$ series is also acceptable, though not nearly so convincing as the $ns\sigma_g$ series.

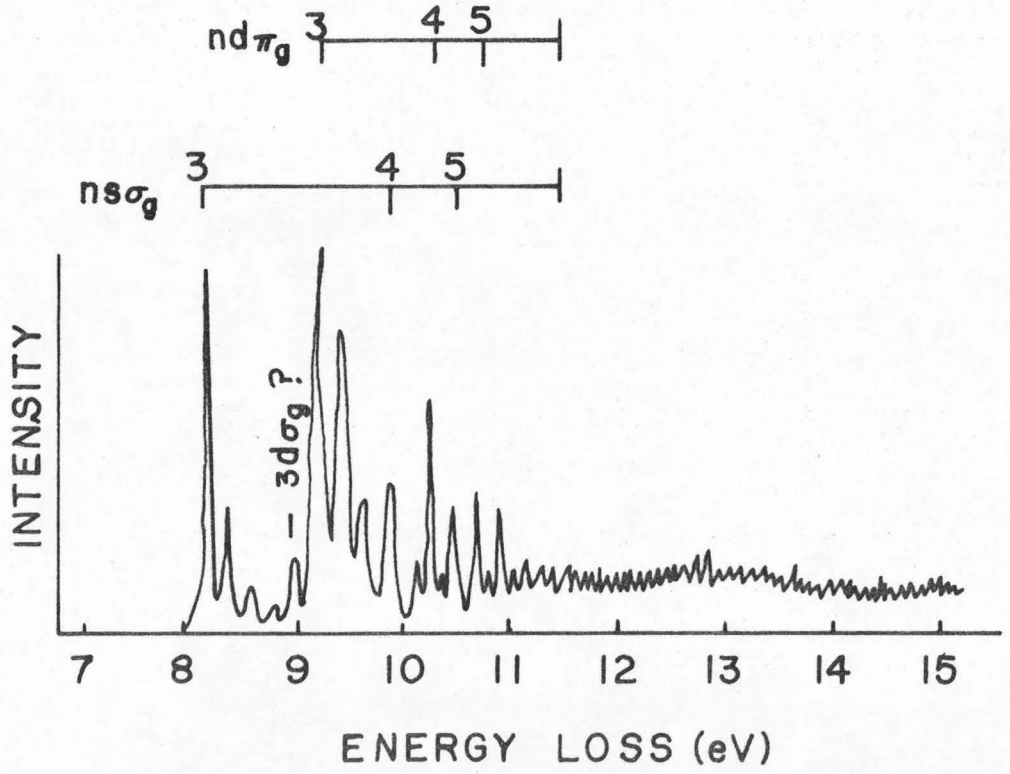


Figure 2. Electron Impact Spectrum of Acetylene

References

1. R. J. Buenker, S. D. Peyerimhoff and J. L. Whitten, J. Chem. Phys. 46, 2029 (1967).
2. G. Herzberg, Disc. Far. Soc. 35, 7 (1963).
3. W. C. Price, Phys. Rev. 47, 444 (1935).
4. P. G. Wilkinson, J. Mol. Spec. 2, 387 (1958).
5. T. Nakayama and K. Watanabe, J. Chem. Phys. 40, 558 (1964).
6. E. N. Lassettre, A. Skerbele, M. A. Dillon and K. J. Ross, J. Chem. Phys. 48, 5066 (1968).
7. E. W. Greene Jr., J. Barnard, A. B. F. Duncan, J. Chem. Phys. 54, 71 (1971).

4.9 FORMALDEHYDE

The ground state of formaldehyde $\tilde{X}(^1A_1)$ belongs to the symmetry group C_{2v}. While there is some spectroscopic evidence to the effect that the Rydberg states of this molecule are non-planar, we shall assume that they belong to the symmetry group C_{2v} also. With this assumption the selection rules for dipole allowed transitions become:

$^1B_1 \leftarrow \tilde{X}$ x transition

$^1B_2 \leftarrow \tilde{X}$ y transition

$^1A_1 \leftarrow \tilde{X}$ z transition

From microwave spectroscopy we find that the ground state $\tilde{X}$ has the following geometry:

C—H 2.082 a.u. ∠ HCH 121.1°

C=O 2.286 a.u.

The orbital energies for formaldehyde have been calculated by several investigators. Their results can be summarized by a table taken from Neumann and Moskowitz.[1]

	Newton and Palke	Foster and Boys	Hornback	Neumann and Moskowitz	
$1a_1$	-20.6237	-20.5897	-20.61869	-20.57293	-20.57379
$2a_1$	-11.4026	-11.3565	-11.37080	-11.34929	-11.34312
$3a_1$	- 1.3977	- 1.3694	- 1.41289	- 1.40280	- 1.40381
$4a_1$	- 0.8314	- 0.8369	- 0.85342	- 0.86412	- 0.86457

$5a_1$	- 0.5932	- 0.5709	- 0.63266	- 0.64901	- 0.65058
$1b_1$	- 0.4971	- 0.4698	- 0.52874	- 0.53307	- 0.53412
$1b_2$	- 0.6759	- 0.6745	- 0.69348	- 0.68830	- 0.68928
$2b_2$	- 0.3955	- 0.3854	- 0.42962	- 0.43919	- 0.44017
E_T	-113.4272	-113.4496	-113.4802	-113.8885	-113.8917
R_{CO}	2.2864	2.30	2.2825	2.2825	2.2825
R_{CH}	2.1164	2.0	2.1090	2.1090	2.1090
$<$ HCH	118°	120°	116.5°	116.5°	116.5°

Thus, we can write the electronic configuration of the ground state $\tilde{X}$ as:

$$\{\text{core}\}\ (2b_2)^2 - {}^1A_1$$

where $\{\text{core}\}$ includes the orbitals:

$$(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(1b_2)^2(5a_1)^2(1b_1)^2$$

and the electronic configuration of the Rydberg states as:

$$\{\text{core}\}(2b_2)(nR)$$

Those Rydberg states which are dipole allowed will be: ${}^1B_1(a_2)$; ${}^1B_2(a_1)$ and ${}^1A_1(b_2)$, where the symmetry in parenthesis is the symmetry of the Rydberg orbital.

The optical spectrum of formaldehyde can be divided into two regions. The long wavelength region from 3530 Å to 2300 Å in the near ultraviolet has been extensively studied and consists mostly

of bands due to a non-planar excited state $\tilde{A}(\{core\}(2b_2)(2b_1)) \leftarrow \tilde{X}$. A weak triplet $\tilde{a}(\{core\}(2b_2)(2b_1)) \leftarrow \tilde{X}$ transition has also been observed in this region. Between 2300 Å and 1750 Å there is no observed absorption.

In the region 1750 Å to 1140Å there are four observed Rydberg series:[2]

87809 - $R/(n - 1.04)^2$

n		I.P. - ν
(3)	$\tilde{B}$	3.802
(4)	$\tilde{F}$	1.631
(5)		.868[a]
(6)		.553[a]

I.P. = 10.885 eV

87830 - $R/(n - .40)^2$

n		I.P. - ν
(3)	$\tilde{E}$	2.013
(4)		1.042[b]
(5)		.633[b]
(6)		.429[b]

I.P. = 10.886 eV

87710 - $R/(n - .70)^2$

n		I.P. - ν
(3)	$\tilde{C}$	2.906
(4)	$\tilde{G}$	1.292
(5)		.738[b]
(6)		.483[b]

I.P. = 10.871 eV

87710 - $R/(n - .70)^2$

n		I.P. - ν
(3)	$\tilde{D}$	2.736
(4)	$\tilde{H}$	1.248
(5)		.738[b]
(6)		.483[b]

I.P. = 10.871 eV

[a] Term values calculated from formula.

[b] As measured by Price.

Some vibrational structure has been observed by Allison and Walsh for the first two members of the Rydberg series with δ = 1.04 and .40. The evidence suggests that n = 3 member of the δ = 1.04 series may be non-planar. The other members of the above series are assumed to be planar.

The results of model calculations on Formaldehyde are as follows:

$a_1(ns\sigma)$, δ = 1.08	$a_1(np\sigma)$, δ = .73	$a_1(nd\sigma)$, δ = .60
3.667	2.643	2.366
1.567	1.315	1.173
.863	.772	.711
.520	.476	
$b_2(np\pi)$, δ = .71	$b_2(nd\pi)$, δ = .54	
2.585	2.248	
1.248		
.768		
.466		

The basis sets used in these calculations were as follows. The two hydrogen atoms were neglected, reducing the problem to a diatomic C=O with $C_{\infty v}$ symmetry (the symmetry of each orbital in the group $C_{\infty v}$ has been placed in paranthesis above). Gaussian functions were put at centers located on the atomic centers themselves, at the mid-point of the molecule and at centers 3.0 a.u. outside of the atomic centers on the molecular axis. For the nsσ and npσ orbital calculations

these were:

Center	Exponent	Type
Carbon, Oxygen	.45	s and p_z
	.15	
Midpoint	.05	s and p_z
	.0166	
	.0055	
	.0018	
	.0006	

For the npπ and ndπ orbital calculations they were:

Center	Exponent	Type
Carbon, Oxygen	.15	p_x
	.05	
	.0166	
	.0055	
Midpoint	.0018	p_x
	.0006	
	.0002	

Finally, for the ndσ orbital calculations they were:

Center	Exponent	Type
Carbon, Oxygen	.45	p_z

	.15	
	.05	
Outside	.0166	p_z
Centers	.0055	
	.0018	
	.0006	
	.0002	

Comparing the results of experiment with the calculations we can identify the $\delta = 1.04$ series as due to transitions to $ns\sigma$, $^1B_2(a_1)$ states. The two $\delta = .70$ series with first members at 64264 cm^{-1} and 65634 cm^{-1} can be identified with the two dipole allowed series $np\sigma$, $^1B_2(a_1)$ and $np\pi$, $^1A_1(b_2)$ respectively. The only other assignment left for the $\delta = .40$ series is with a $nd\sigma$, $^1B_2(a_1)$, an $nd\pi$, $^1A_1(b_2)$ or a $nd\delta$, $^1B_1(a_2)$ series, all of which are dipole allowed. Only the first two of these series have been calculated, but one expects that the quantum defect of the $nd\delta$ series will approximate that of the $nd\pi$ series and thus be fairly large.

Our assignment agrees with that given by Herzberg.[3] He finds the nd assignment difficult to make because of the large quantum defect $\delta = .40$. Our model calculations do give large quantum defects for the nd series, a result that is difficult to predict beforehand.

References

1. D. B. Neumann and J. W. Moskowitz, J. Chem. Phys. 50, 2216 (1969).

2. W. C. Price, J. Chem. Phys. 3, 256 (1935).
K. Allison and A. D. Walsh, Chem. Inst. of Canada Symposium, Ottawa (1957).

3. G. Herzberg, Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand, New York (1966), p. 522.

4.10 FORMIC ACID

The ground state of formic acid $\tilde{X}$ is planar C_s, and we shall assume that the same is true of its excited states. The selection rules for dipole allowed transitions from the ground state are then:

$^1A'' \leftarrow \tilde{X}$ z transition

$^1A' \leftarrow \tilde{X}$ x, y transition

Infrared and microwave spectroscopy give the following geometrical parameters of the ground state $\tilde{X}$.

C=O ~ 2.271 a.u. ∠OCO ~ 124.9°

C–O ~ 2.538 a.u. ∠HCO ~ 124.1°

C–H ~ 2.073 a.u. ∠COH ~ 106.3°

O–H ~ 1.837 a.u.

The orbital energies for formic acid have been calculated by Peyerimhoff and Buenker[1] and by Basch, Robin and Kuebler.[2] The results of their calculations are as follows:

	Peyerimhoff and Buenker		Basch et al.
1a′	-20.5926	-20.6344	-20.625
2a′	-20.5529	-20.5831	-20.582
3a′	-11.5818	-11.4759	-11.430
4a′	- 1.5091	- 1.5271	- 1.511

	Peyerimhoff and Buenker		Basch et al.
5a′	- 1.3852	- 1.3931	- 1.404
6a′	- 0.9209	- 0.9337	- 0.908
7a′	- 0.7548	- 0.7606	- 0.741
8a′	- 0.7102	- 0.7246	- 0.714
1a″	- 0.6654	- 0.6608	- 0.652
9a′	- 0.5785	- 0.5963	- 0.602
10a′	- 0.4902	- 0.4916	- 0.500(2a″)
2a″	- 0.4809	- 0.4897	- 0.481(10a′)

corresponding to total energies of -188.4985, -188.6552 and -188.6877, respectively.

Thus the electronic configuration of the ground state $\tilde{X}$ of formic acid is:

$$\{\text{core}\}(2a'')^2 - {}^1A'$$

where $\{\text{core}\}$ represents the orbitals:

$$(1a')^2(2a')^2(3a')^2(4a')^2(5a')^2(6a')^2(7a')^2(8a')^2(1a'')^2 \times (9a')^2(10a')^2$$

and the electronic configuration of the Rydberg series converging to the lowest ionization limit will be:

$$\{\text{core}\}(2a'')(nR)$$

Wee see that the Rydberg orbital may have either symmetry a′ or a″ and still be dipole allowed.

The optical spectrum of formic acid begins at about 2600 Å. The region of 2250 Å to 2600 Å consisting of indistinct bands merging into a continuum has been assigned to the transition $\tilde{A}\ [\{core\}(2a'')(3a'')] \leftarrow \tilde{X}$.

The next region of absorption is that below 1550 Å. From 1400 Å to 1100 Å Price and Evans[3] observed a series of sharp bands converging to a continuum which they assigned as a Rydberg series:

$$91370 - R/(n - .60)^2$$

n		I.P. - ν
(3)	$\tilde{C}$	2.375
(4)	$\tilde{F}$	1.176
(5)		.703
(6)		.459

I.P. = 11.325 eV

They also observed diffuse bands in this region, in particular one at 64500 cm^{-1} or 3.33 eV below the ionization potential.

The results of model calculations on formic acid are as follows:

a′, δ = 1.00	a′, δ = .86	a′, δ = .50
3.387	2.959	2.170
1.487	1.358	
.834		
.512		

a″, δ = .66	a″, δ = .06
2.489	1.569
1.223	

The basis sets used were as follows. For the purposes of calculation, the hydrogens were neglected leaving a bent CO_2 core. Gaussian functions were placed at each of the atomic centers and at the center of gravity of the CO_2 core, assuming each atom to have unit mass. For the a′ orbital calculations these functions were:

Center	Exponent	Type
Oxygens	.45	s
Carbon	.45	s
Center of Gravity	.45	s, p_x and p_z
	.15	
	.05	
	.0166	
	.0055	
	.0018	
	.0006	

For the a″ orbital calculations they were:

Carbon, Oxygens	.45	p_y
	.15	
	.05	
	.0166	
	.0055	

The optical spectrum can be interpreted as follows on the basis of our calculations.

The Rydberg series observed by Price and Evans fits best with the a″ series with quantum defect $\delta = .66$. We would interpret this series as a 'P' like series, perpendicular to the plane of the molecule, Price and Evans interpret it as a transition of a lone pair electron from the oxygen in the C=O double bond. These interpretations are not necessarily different. Thus the Rydberg states in this series can be assigned as $^1A'(a'')$ where the symmetry in parenthesis is the symmetry of the Rydberg orbital.

The diffuse band at 64500 cm^{-1} could be the first member of another a′ Rydberg series. We would interpret this series as an 's' like series, and assign the state at 64500 cm^{-1} as $^1A''(a')$. The fact that this transition is very different in appearance from the $^1A'(a'')$ transitions lends support to this interpretation. The diffuse nature of the series could be responsible for the non-appearance of the other expected members of the series.

Basch, Robin and Kuebler have made a general study of several amides, carboxylic acids and acyl fluorides. The conclusions above are in agreement with the conclusions these authors make for the above class of molecules.

REFERENCES

1. S. D. Peyerimhoff and R. J. Buenker, J. Chem. Phys., 50, 1846 (1969).

2. H. Basch, M. B. Robin, N. A. Kuebler, J. Chem. Phys., 49, 5007.

3. W. C. Price, W. M. Evans, Proc. Roy. Soc., 162A, 110 (1937).

4.11 DIAZOMETHANE

The ground state of diazomethane $\tilde{X}$ is planar (C_{2v}) and the same seems to be true of its Rydberg states. Thus the selection rules for dipole allowed transitions to the ground state are:

$^1B_1 \leftarrow \tilde{X}$	x transition
$^1B_2 \leftarrow \tilde{X}$	y transition
$^1A_1 \leftarrow \tilde{X}$	z transition

Infrared and microwave spectroscopy yield the following geometrical parameters for the ground state.

N=N ~ 2.117 a.u.	C–H ~ 2.041 a.u.
C=N ~ 2.494 a.u.	∠ HCH ~ 127°

The orbital energies for diazomethane have been calculated by André, André, Leroy and Weiler.[1] Their results are listed below.

$1a_1$	-15.9635
$2a_1$	-15.7969
$3a_1$	-11.3854
$4a_1$	- 1.5409
$5a_1$	- 1.1410
$6a_1$	- 0.9161
$1b_2$	- 0.7304
$1b_1$	- 0.7304
$7a_1$	- 0.6814

$2b_2$	- 0.4604
$2b_1$	- 0.3734
$3b_2$	0.0996

Thus the electronic configuration for the ground state $\tilde{X}$ of diazomethane is:

$$\{core\}(2b_1)^2 - {}^1A_1$$

where $\{core\}$ represents the orbitals:

$$(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(5a_1)^2(6a_1)^2(1b_2)^2(1b_1)^2(7a_1)^2(2b_2)^2$$

The electronic configuration of the Rydberg states converging to the lowest ionization limit of diazomethane will be:

$$\{core\}(2b_1)(nR)$$

and the dipole allowed transitions are ${}^1B_1(a_1)$, ${}^1B_2(a_2)$ and ${}^1A_1(b_1)$, where the symmetry in parenthesis is the symmetry of the Rydberg orbital.

The optical spectrum of diazomethane starts with a weak absorption below 4750 Å which is responsible for the yellow color of diazomethane gas. Between 4750 Å and 3200 Å there are a series of discrete bands merging into a continuum with a maximum at 3950 Å. This band has been ascribed to the transition $\tilde{A}(\{core\}(2b_1)(3b_2)?) \leftarrow \tilde{X}$. A second stronger absorption between 2650 Å and 2000 Å with maximum at 2175 Å is ascribed to a second transition $\tilde{B}(\{core\}(2b_1)(3b_1)?) \leftarrow \tilde{X}$.

In the region below 2100 Å only discrete bands are found. Merer[2] has performed a detailed analysis of bands in the region 1930 Å to 1780 Å and finds them to be mainly ⊥ bands, two of type $^1B_1 \leftarrow \tilde{X}$ and one of type $^1B_2 \leftarrow \tilde{X}$. The fact that ∥ components are weakly present in these transitions suggests that the molecule is planar C_{2v} in these excited states.

Merer also observed a Rydberg series in this region with the following formula:

$$72585 - R/(n - .10)^2$$

n	I.P. - ν
(3)	1.623
(4)	.893
(5)	.568

I.P. = 8.997 eV

The n = 3 member of this series appears to be a ∥ transition analogous to the case of ketene.

In addition to the above bands, there is observed a system of ⊥ bands in the region of 1585 Å, 1.21 eV below the ionization limit. This system together with those of the 1900 Å region, 2.48 eV below the ionization limit have been suggested as the first two members of an npσ series with quantum defect δ = .67 by Merer.

Finally, at 1750 Å, 1.95 eV below the ionization limit there is a group of diffuse bands which do not seem to belong to any Rydberg series.

Model calculations on diazomethane give the following results.

$a_1(ns\sigma)$, $\delta = .98$	$a_1(np\sigma)$, $\delta = .58$	$a_1(nd\sigma)$, $\delta = .71$
3.338	2.325	2.597
1.505	1.137	1.365
.850	.682	.705
.525	.446	

$b_1(np\pi)$, $\delta = .66$	$b_1(nd\pi)$, $\delta = .03$
2.471	1.542
1.214	.991
.737	.635
.470	

The basis sets used in these calculations are as follows. For the purposes of calculation the hydrogens were neglected, so that only a linear C=N=N core was considered. The symmetry of the orbitals for this $C_{\infty v}$ core is given in parenthesis above. Gaussian basis functions were placed at centers located on the atomic centers and at extended centers 3.0 a.u. to either side of the atomic centers on the molecular axis. For the $ns\sigma$ and $np\sigma$ orbital calculations these functions were:

Center	Exponent	Type
End Nitrogen }	.45	s and p_z
Carbon }	.15	
	.05	

Center	Exponent	Type
Center Nitrogen	.0166	s and p_z
	.0055	
	.0018	
	.0006	
	.0002	

For the npπ orbital calculations they were:

Center	Exponent	Type
End Nitrogen, Carbon	.45	p_x
	.15	
	.05	
	.0166	
	.0055	
	.0018	
	.0006	
Center Nitrogen	.45	p_x
	.15	
	.05	

For the ndσ orbital calculations they were:

Center	Exponent	Type
End Nitrogen }	.45	p_z
Carbon }	.15	
	.05	
	.0166	
	.0055	
	.0018	
	.0006	
Center Nitrogen	.45	p_z
	.15	
	.05	

Finally, for the ndπ orbital calculations they were:

Center	Exponent	Type
End Nitrogen }	.45	p_x
Carbon }	.15	
	.05	
	.0166	
Extended Centers	.0055	p_x
	.0018	
	.0006	
	.0002	

Just as the optical spectra of diazomethane and ketene are practically the same, their interpretation is practically the same also.

We recognize Merer's series as an ndπ series and not an nsσ series. This identification is made because of the absence of an n = 2 member for the series, and because of the experimental

observation that the series is made up of ∥ bands. Thus, these states are $^1A_1(b_1)$ states.

Where we suggested the existence of a second series in ketene Merer has suggested the existence of an npσ in diazomethane. Our calculations show that an npσ series fits very well with the experimental data. We assign these states as $^1B_1(a_1)$ states. This suggests that the series in ketene is an npσ series too.

REFERENCES

1. J. M. André, M. Cl. André, G. Leroy and J. Weiler, Int. J. Quant. Chem., 3, 1013 (1969).
2. A. J. Merer, Can. J. Phys., 42, 1242 (1964).

4.12 KETENE

The ground state of ketene $\tilde{X}$ is planar (C_{2v}); and while some of the excited states may be non-planar, the Rydberg states of ketene, since their spectroscopic fine structure has not been as yet resolved, will be assumed to be planar also. Thus, the dipole-allowed transitions to the ground state are:

$^1B_1 \leftarrow \tilde{X}$	x transition
$^1B_2 \leftarrow \tilde{X}$	y transition
$^1A_1 \leftarrow \tilde{X}$	z transition

Infrared and microwave spectroscopy give the following geometrical parameters of the ground state $\tilde{X}$.

C=O ~ 2.192 a.u.	C-H ~ 2.039 a.u.
C=C ~ 2.485 a.u.	∠ HCH ~ 123.3°

The orbital energies for ketene have been calculated by Letcher, Unland and Van Wazer.[1] Their orbital energies are as follows:

$1a_1$	-20.655441
$2a_1$	-11.395302
$3a_1$	-11.233078
$4a_1$	- 1.499226
$5a_1$	- 1.053224
$6a_1$	- 0.740288
$7a_1$	- 0.661053

$1b_2$	- 0.653645
$1b_1$	- 0.634406
$2b_2$	- 0.546228
$2b_1$	- 0.343962

corresponding to a total energy of -151.507701.

Thus, the electronic configuration of the ground state $\tilde{X}$ of ketene is:

$$\{\text{core}\}(2b_1)^2 - {}^1A_1$$

where $\{\text{core}\}$ represents the orbitals:

$$(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(5a_1)^2(6a_1)^2(7a_1)^2(1b_2)^2(1b_1)^2(2b_2)^2$$

The electronic configuration of the lowest lying Rydberg states is expected to be:

$$\{\text{core}\}(2b_1)(nR)$$

and the dipole allowed transitions from the ground state are ${}^1B_1(a_1)$, ${}^1B_2(a_2)$ and ${}^1A_1(b_1)$, where the symmetry in parenthesis is the symmetry of the Rydberg orbital.

Ketene is iso-electronic with carbon dioxide, however, its optical spectrum bears little resemblance to the spectrum of carbon dioxide.

The first absorption for ketene begins in the region 3850 Å to 2600 Å and has been assigned to a transition $\tilde{A}(\{\text{core}\}(2b_1)(3b_2)?) \leftarrow \tilde{X}$ to a non-planar excited state of ketene. Another absorption in the

region 2130 Å to 1930 Å has been assigned to a second excited state transition $\tilde{B}(\{core\}(2b_1)(3b_1)?) \leftarrow \tilde{X}$.

When we proceed to the region beyond 1850 Å we meet with a system of several very strong discrete absorptions, some of which can be fit into a Rydberg series. Price, Teegan and Walsh,[2] have fit four of these bands together with two bands near 1300 Å into the following Rydberg series.

$$77491 - R/(n - 1.07)^2$$

n		I.P. - ν
(3)	$\tilde{C}$	2.828
(4)	$\tilde{E}$	1.578
(5)	$\tilde{G}$	.883
(6)	$\tilde{H}$	.559

I.P. = 9.605 eV

Two other bands are also observed in this region, $\tilde{D}$ at 61550 cm^{-1} and $\tilde{F}$ at 66984 cm^{-1}, or 1.97 eV and 1.30 eV below the ionization limit at 77491 cm^{-1}.

Herzberg[3] has argued from the appearance of the bands that they are all due to $\parallel$ transitions, i.e., $^1A_1 \leftarrow \tilde{X}$. He states "It is probable that the observed features represent Q branches of unresolved $\parallel$ bands. For $\perp$ bands, since A is large, the k structure would have been easily resolved... The $\perp$ transitions which are expected are probably forming an unresolved background in the spectrum." We will have more to say about this after we have examined the results of our model calculations.

The actual results of these calculations are as follows:

$a_1(ns\sigma)$, $\delta = .96$	$a_1(np\sigma)$, $\delta = .59$	$a_1(nd\sigma)$, $\delta = .70$
3.263	2.339	2.557
1.462	1.144	1.315
.829	.687	.706
.517	.448	

$b_1(np\pi)$, $\delta = .63$	$b_1(nd\pi)$, $\delta = -.06$
2.437	1.394
1.120	.847
.731	
.469	

The basis sets used are given below. For the purpose of calculation the hydrogens were neglected leaving a C=C=O core. The symmetry of the orbitals as calculated is given in parenthesis above. Gaussian basis functions were placed at centers located on the atomic centers and extended centers 3.0 a.u. to either side of the atomic centers on the molecular axis. For the $ns\sigma$ and $np\sigma$ orbital calculations these functions were:

Center	Exponent	Type
End Carbon }	.45	s and p_z
Oxygen }	.15	
	.05	

Center	Exponent	Type
Center Carbon	.0166	s and p_z
	.0055	
	.0018	
	.0006	
	.0002	

For the npπ orbital calculation they were:

Center	Exponent	Type
End Carbon, Oxygen	.45	p_x
	.15	
	.05	
	.0166	
	.0055	
	.0018	
	.0006	
Center Carbon	.45	p_x
	.15	
	.05	

For the ndσ orbital calculation they were:

Center	Exponent	Type
End Carbon, Oxygen	.45	p_z
	.15	
	.05	
	.0166	
	.0055	
	.0018	
	.0006	
Center Carbon	.45	p_z
	.15	
	.05	

Finally for the ndπ orbital calculation they were:

Center	Exponent	Type
End Carbon, Oxygen	.45	p_x
	.15	
	.05	
	.0166	
Extended Centers	.0055	p_x
	.0018	
	.0006	
	.0002	

In evaluating the calculated results we must be careful. On first notice the experimental Rydberg series would seem to be an

$a_1(ns\sigma)$ series. However, this would give the Rydberg states $^1B_1$ symmetry which could not correspond to || transitions as Herzberg requires.

To get || transitions we must interpret the series as an $nd\pi$ series. This requires that the quantum defect $\delta \approx .07$ and that we renumber the series. The states are then $^1A_1(b_1)$ states and correspond to || transitions. The question then arises, where does the first member of this series belong? We note that this state at 2.83 eV below the ionization limit together with the state at 66984 cm^{-1}(1.30 eV below the ionization limit) look like the first two members of an $nd\sigma$ or np series. The results for diazomethane suggest that it is an $np\sigma$ series, although the other two possibilities are not absolutely ruled out.

We tentatively identify these states as the first two members of a $^1B_1(a_1)$ series with quantum defect $\delta \approx .81$.

The assignments which we have made above receive added support from the interpretation of the diazomethane spectrum. The spectra and interpretation of the ketene and diazomethane spectra are practically identical. For the case of diazomethane, Herzberg's comments on the nature of the transitions have been confirmed by Merer.[4] Furthermore, our own calculations on diazomethane agree much better with the experimental values than they do for ketene. We are, therefore, convinced that the interpretations which we have given above are the correct ones.

REFERENCES

1. J. H. Letcher, M. L. Unland, J. R. Van Wazer, J. Chem. Phys., 50, 2185 (1969).
2. W. C. Price, J. P. Teegan and A. D. Walsh, J. Amer. Chem. Soc., 920, (1951).
3. G. Herzberg, Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand, New York (1966), p. 530.
4. A. J. Merer, Can. J. Phys., 42, 1242 (1964).

4.13 ETHYLENE

The ground state of ethylene $\tilde{X}$ (^1A_g) is planar and of symmetry D_{2h}. While some of the excited states of ethylene including the Rydberg state at 7.1 eV are nonplanar,[1] we shall assume that the remaining Rydberg states with which we have to deal are of symmetry D_{2h} also. With this assumption the selection rules for dipole allowed transitions from the ground state $\tilde{X}$ are:

$^1B_{3u} \leftarrow \tilde{X}$ x transition

$^1B_{2u} \leftarrow \tilde{X}$ y transition

$^1B_{1u} \leftarrow \tilde{X}$ z transition

Infrared and raman spectroscopy on the ground state $\tilde{X}$ of ethylene yield the following geometrical parameters:

C-H $\sim$ 2.052 a.u. $\quad \angle HCH \sim 117.6°$

C-C $\sim$ 2.530 a.u.

The orbital energies for ethylene have been calculated by many investigators. To illustrate the general kinds of results obtained we give part of a table from Kaldor and Shavitt.[2]

	Without σ-π exchange	Complete treatment
$1a_g$	-11.3024	-11.2794
$1b_{1u}$	-11.3020	-11.2787
$2a_g$	-0.9444	-1.0130

	Without σ-π exchange	Complete treatment
$2b_{1u}$	-0.7575	-0.7815
$1b_{2u}$	-0.6366	-0.6431
$3a_g$	-0.5516	-0.5605
$1b_{3g}$	-0.5033	-0.5054
$1b_{3u}$	-0.2170	-0.3690
E_T	-77.5035	-77.8355

In the above, the symmetry designations of the orbitals have been changed from those of Kaldor and Shavitt[2] to conform to our choice of coordinate system.

The electronic configuration of the ground state $\tilde{X}$ of ethylene can be written as:

$$\{\text{core}\}\,(1b_{3u})^2 \; - \; {}^1A_g$$

where {core} represents the orbitals:

$$(1a_g)^2(1b_{1u})^2(2a_g)^2(2b_{1u})^2(1b_{2u})^2(3a_g)^2(1b_{3g})^2.$$

The electronic configuration of the Rydberg states converging to the first ionization limit of ethylene can be written as:

$$\{\text{core}\}\,(1b_{3u})(nR).$$

Thus, the dipole allowed transitions from the ground state will be ${}^1B_{3u}\,(a_g)$, ${}^1B_{2u}\,(b_{1g})$ and ${}^1B_{1u}\,(b_{2g})$, where the symmetry in parentheses is the symmetry of the Rydberg orbital.

The ethylene optical spectrum begins with an extremely weak absorption in the region 3400 Å to 2600 Å. The diffuse bands of this progression have been attributed to the transition $\tilde{a}\ [\{core\}(1b_{3u})(1b_{2g})\ -\ {}^3B_{1u}] \leftarrow \tilde{X}$. This state is frequently called the T state.

Another stronger continuum beginning at 2600 Å and extending through 1750 Å has been assigned to the singlet state of the same electronic configuration $\tilde{A}\ [\{core\}(1b_{3u})(1b_{2g})\ -\ {}^1B_{1u}] \leftarrow \tilde{X}$. This state is called the V state.

Beginning at 1740 Å there is a system of sharp bands, extending up to 1200 Å, which have been assigned to four different Rydberg series by Wilkinson.[3] These series are:

R		R′	
$84750 - R/(n - 1.09)^2$		$84750 - R/(n - .6)^2$	
n	I.P. − ν	n	I.P. − ν
(3)	3.398	(3)	2.249
(4)	1.607	(4)	1.145
(5)	.885	(5)	.70 [a]
(6)	.56 [a]	(6)	.47 [a]
I.P. = 10.504		I.P. = 10.504	

R″		R‴	
$84750 - R/(n - .4)^2$			
n	I.P. - ν	n	I.P. - ν
(3)	1.888	(3)	1.455
(4)	.994		
(5)	.64 [a]		
	I.P. = 10.504		

[a] Calculated from formula.

The results of model calculations on ethylene are as follows:

$a_g(ns\sigma)$, $\delta = 1.00$	$a_g(nd\sigma)$, $\delta = .58$	np, $\delta = .67$
3.42	2.32	2.50
1.49	1.15	1.23
.84	.60	.74
.51		

$b_{2g}(nd\pi)$, $\delta = 0.0$	$b_{1g}(nd\delta)$, $\delta = 0.0$
1.52	1.51
.99	.99
.53	.54

In the above table the $np\sigma$ and $np\pi$ orbital calculations are so similar that we have grouped them under the common heading np.

The basis sets used were as follows. The hydrogen atoms were neglected, leaving a C=C ($C_{\infty v}$) core. The actual symmetries of the orbitals as calculated have been placed in parentheses in the above table. Gaussian functions were placed at the atomic centers, at the midpoint of the core, and at points 3.0 a.u. to either side of the atomic centers on the core axis. For the nsσ and npσ orbitals these functions were:

Center	Exponent	Type
Carbons	.45	s and p_z
	.15	
Midpoint	.05	s and p_z
	.0166	
	.0055	
	.0018	
	.0006	

For the ndσ orbital calculations they were:

Center	Exponent	Type
Carbons	.45	p_z
	.15	
	.05	
Extended Centers	.0166	p_z
	.0055	
	.0018	
	.0006	

Finally for the $np\pi$ and $nd\pi$ orbitals these functions were:

Center	Exponent	Type
Carbons	.15	p_x
	.05	
	.0166	
Extended Centers	.0055	p_x
	.0018	
	.0006	

The interpretation of the optical spectrum of ethylene goes as follows:

The experimental R series fits very well with the calculated $a_g(ns\sigma)$ series. These states are then $^1B_{3u}(a_g)$ states.

Again, the experimental R′ series fits with the calculated $a_g(nd\sigma)$ series, and we assign these states as $^1B_{3u}(a_g)$ also.

The R series does not fit well with any of the series we have calculated. Since there is one dipole allowed series which we have not calculated, the $a_g(nd\delta)$ series, we suspect that the R″ series might be this series. Merer and Mulliken[4] favor this kind of assignment on other grounds, since, they argue, for n = 3 only the transitions to $3d\delta$ orbitals can occur, because the UAO's $3d\sigma$, $3d\pi_x$ and $3d\pi_y$ correspond to the occupied valence shell MO's $3a_g$, $1b_{3g}$, $1b_{2g}$. However, we must point out that according to our calculations the $3d\sigma$ transition does occur, contrary to their prediction. If we assign the R″ series as $a_g(nd\delta)$ then these states are $^1B_{3u}(a_g)$.

The R''' series is represented by a single member 1.47 eV below the ionization potential. We assign this series as $b_{2g}(nd\pi)$. If this assignment were made on the basis of the experimental spectrum alone, it would be quite tentative. However, there are Hartree-Fock calculations which can be interpreted as supporting our conclusions. We shall discuss these presently. The R''' series corresponds then to $^1B_{1u}(b_{2g})$ states.

Finally Wilkinson tentatively assigned states at 8.92, 9.11 and 9.39 eV as members of a possible fifth nR'''' series. These give term values of 1.60, 1.41 and 1.13 eV respectively. We propose that the state at 9.11 eV is probably a vibrational member of the $4R'''$ series and therefore assign the states with term values 1.60 and 1.13 eV to a nR''' series, $n = 3, 4...$ corresponding to the $b_{1g}(nd\delta)$ orbitals. This would then account for the last of the five dipole allowed Rydberg series possible in ethylene. These states would then be $^1B_{2u}(b_{1g})$.

Transitions to states with configuration $\{core\}(1b_{3u})(np\sigma)$ or $\{core\}(1b_{3u})(np\pi)$ are dipole forbidden. For example the $np\sigma$ series would correspond to the electric quadrupole allowed transition $^1B_{2g} \leftarrow \tilde{X}$. From our calculated term values there should be $^1B_{1g}$, $^1B_{2g}$ and ^1A_g states at 8.0 eV. The existence of these states may be a part of the explanation of the minimum in the generalized oscillator strength as a function of momentum transfer, f(K), recently observed in the electron impact spectrum of ethylene. It can be shown that Rydberg and valence transitions can be distinguished by the appearance of a minimum in the curve for f(K) for

Rydberg transitions while for valence transitions f(K) should decrease monotonically as K increases.[5] This argument is based on the presence or absence of radial nodes in the molecular orbitals involved in the transition. Krauss and Mielczarek[6] have used this characteristic minimum to study the Rydberg character of the excited states corresponding to energy losses of 7.16, 8.0, 8.17 and 9.12 eV. The energy losses at 7.16, 8.17 and 9.12 clearly correspond to Rydberg transitions $\pi \rightarrow 3s$, $\pi \rightarrow 4d\sigma$ and $\pi \rightarrow 4s$ with calculated term values 3.4, 2.3 and 1.5 eV respectively. In agreement with the theoretical curves minima are observed in f(K) for these three energy losses. To study the orbital character of the V state Krauss and Mielczarek chose an energy loss of 8 eV due to the Rydberg peaks lying on top of the N → V absorption. The f(K) curve for this energy loss shows a minimum. This is surprising since the V state, with its strong oscillator strength, is usually identified with a valence transition and, like its UAO limit $2p_x \rightarrow 3d\pi$, involves orbitals with no radial nodes. One explanation is that the Rydberg contribution at an energy loss of 8.0 eV is due to dipole-forbidden Rydberg transitions that become allowed as the molecule becomes nonplanar. Our calculations support this explanation since they show three Rydberg states $\pi \rightarrow 3p_x$, $3p_y$ and $3p_z$ at about 8.0 eV, all of which become allowed as the molecule is distorted from the planar geometry. The energy of these Rydberg states will change very little as the CH_2 groups twist relative to each other and hence should still be around 8.0 eV.

The other explanation, namely that there is configurational mixing of considerable Rydberg character with the valence state is still a possibility.

We predict $^1B_{1u}$ Rydberg states $\{core\}(1b_{3u})(nd\pi_x)$ with term values of 1.52, 0.99 and 0.53 eV. These states are of the same symmetry as the V state. Experimentally the first member should therefore be at 9 eV. However, direct SCF calculations on the C_2H_4 ground state and the $C_2H_4^+$ ion give an SCF ionization potential of 9.03 eV.[7] Therefore, in the Hartree-Fock approximation we can expect these $^1B_{1u}$ Rydberg states to be at 7.51, 8.04 and 8.50 eV if our calculations are correct. Direct SCF calculations with a large basis flexible enough to describe both the valence (π, π^*) state and the Rydberg states $(\pi, nd\pi_x)$ give states at 7.43, 8.13 and 8.64 eV.[8] Surprisingly, no valence-like (π, π^*) state emerges from these calculations. All the states are clearly very diffuse, e.g., the state at 7.43 eV has an orbital with the matrix element $\langle x^2 \rangle$ = 42 a.u.^{2}. It becomes obvious that only Rydberg states emerge from the SCF approximation and that in this same approximation the valence-like state probably lies above the energy of the positive ion.

The electron impact spectrum of ethylene has been observed by Lassettre, et al.[9] Their spectrum together with our assignments is reproduced in Figure 1.

It is clear from looking at the electron impact spectrum that it shows the same transitions as the optical spectrum. The $ns\sigma_g$ and $nd\sigma_g$ series are especially prominent.

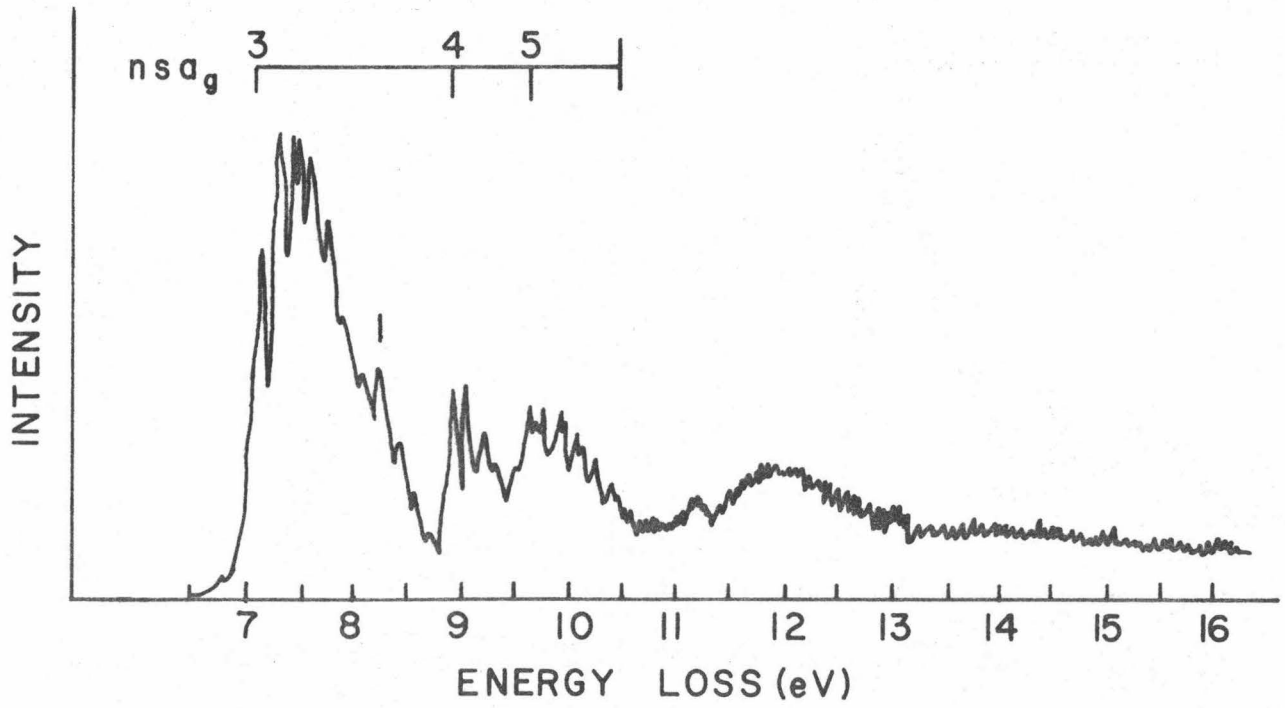


Figure 1. Electron Impact Spectrum of Ethylene

It remains for us to compare our assignments with those of Bélanger and Sandorfy.[10] These authors measured the vacuum ultraviolet spectra of the complete series of fluoroethanes from 2000 Å to 1150 Å. They observed a $\pi^* \leftarrow \pi$ transition and three different Rydberg series in all of the spectra. The quantum defects of the three series are given in the table below.

	nR	nR′	nR″
monofluoroethylene	.90	.40	.03
1, 1-difluoroethylene	.96	.49	.02
trans-1, 2-difluoroethylene	.89	.48	.07
cis-1, 2-difluoroethylene	.97	.52	.17
trifluoroethylene	.90	.44	.01
tetrafluoroethylene	.99	.58	.05

It is obvious that the different Rydberg series correspond to the same Rydberg orbital in the different molecules. Bélanger and Sandorfy assign these with the R series corresponding to ns Rydberg orbitals, the R′ series corresponding to np orbitals, and the R″ series corresponding to nd orbitals.

While we certainly agree with their assignment of the R series as corresponding to ns Rydberg orbitals, we would say, based upon our ethylene calculations, that both the R′ and R″ series correspond to nd orbitals. We do not expect the R′ series to correspond to an np series because even though this series is now dipole allowed for these molecules, we expect its quantum

defect δ to be about .67. This is much larger than the quantum defects of any of the fluoroethylenes for the R′ series. On the other hand, we would expect the quantum defect of the ndσ series to be about .58, and while it is a bit larger than most of the quantum defects of the fluoroethylenes for the R′ series, it is exactly right for tetrafluoroethylene. We then assign the R′ series as corresponding to ndσ orbitals.

The R″ series quantum defects are quite small, and we postulate that these series are analogous not to the R″ series in ethylene, but to the R‴ series. We would then assign the R″ series as observed in the fluoroethylenes as corresponding to ndπ_x orbitals.

References

1. A. J. Merer and L. Schoonveld, Can. J. Phys. 47, 1731 (1969).
2. U. Kaldor and I. Shavitt, J. Chem. Phys. 48, 191 (1968).
3. P. G. Wilkinson, Can. J. Phys. 34, 643 (1956).
4. A. J. Merer and R. S. Mulliken, Chem. Rev. 69, 639 (1969).
5. K. Miller, J. Chem. Phys. 51, 5235 (1969).
6. M. Krauss and S. R. Mielczarek, J. Chem. Phys. 51, 5241 (1969).
7. H. Basch and V. McKoy, J. Chem. Phys. 53, 1628 (1970).
8. T. Dunning, W. Hunt and W. A. Goddard, Chem. Phys. Lett. 4, 147 (1969).
9. E. N. Lassettre, A. Skerbele, M. A. Dillon and K. J. Ross, J. Chem. Phys. 48, 5066 (1968).
10. G. Bélanger and C. Sandorfy, J. Chem. Phys. 55, 2055 (1971).

4.14 ALLENE

The ground state of allene $\tilde{X}(^1A_1)$ is of symmetry D_{2d}, and the same is true presumably of its excited states. Thus, the selection rules for dipole allowed transitions involving the ground state are:

$^1B_2 \leftarrow \tilde{X}$ z transition

$^1E \leftarrow \tilde{X}$ x, y transition

From infrared and raman spectroscopy the following geometrical parameters have been determined for the ground state $\tilde{X}$.

C=C ~ 2.473 a.u.
C—H ~ 2.054 a.u.
$\angle$ HCH ~ 118.2°

The orbital energies of allene have been calculated by Buenker.[1] According to his calculations the orbital energies are:

$1a_1$	-11.4209
$1b_2$	-11.3466
$2a_1$	-11.3465
$3a_1$	-1.1044
$2b_2$	-0.9934
$4a_1$	-0.7389
$3b_2$	-0.6575
1e	-0.6458
2e	-0.4211

while the total energy is -115.6979.

Thus the electronic configuration of the ground state $\tilde{X}$ is:

$$\{\text{core}\}(2e)^4$$

where {core} denotes the orbitals:

$$(1a_1)^2(1b_2)^2(2a_1)^2(3a_1)^2(2b_2)^2(4a_1)^2(3b_2)^2(1e)^4$$

and the electronic configuration of the lowest Rydberg state will be:

$$\{\text{core}\}(2e)^3(nR).$$

All symmetries of Rydberg orbitals will be allowed, since the dipole allowed transitions become: $^1E(a_1)$, $^1E(a_2)$, $^1E(b_1)$, $^1E(b_2)$ and $^1B_2(e)$, the symmetry in parentheses being the symmetry of the Rydberg orbital.

The optical spectrum of allene begins at about 2030 Å. The first part of the spectrum is a continuous absorption with a maximum at 1710 Å, corresponding to a transition $\tilde{A}\ [\{\text{core}\}(2e)^3(3e)] \leftarrow \tilde{X}$. Overlapping part of this continuum is a progression of diffuse bands corresponding to the symmetrical stretching vibration of the C=C bands.

Below 1550 Å Sutcliffe and Walsh[2] have observed strong but diffuse bands that may belong to as many as nine Rydberg series. According to Herzberg,[3] "Some of [these series] are rather fragmentary and probably represent simply vibrational members of the main Rydberg series." As reported by Sutcliffe and Walsh, these series are:

I

$82210 - R/(n - 1.06)^2$

n		I.P. - ν
(3)	$\tilde{B}$	3.026
(4)		1.618
(5)		.875
(6)		.559

I.P. = 10.190 eV

II

$82190 - R/(n - .70)^2$

n		I.P. - ν
(3)	$\tilde{C}$	2.167
(4)		1.253
(5)		.735
(6)		.485

I.P. = 10.187 eV

III

$82190 - R/(n - .55)^2$

n		I.P. - ν
(3)	$\tilde{D}$	2.030
(4)		1.173
(5)		.710
(6)		.454

I.P. = 10.187 eV

IV

$82190 - R/(n - .55)^2$

n		I.P. - ν
(3)	$\tilde{D}$	1.983
(4)		1.128
(5)		.671
(6)		.454

I.P. = 10.187 eV

V

$82200 - R/(n - .40)^2$

n		I.P. - ν
(3)	$\tilde{E}$	1.870
(4)		1.051
(5)		.637

I.P. = 10.188 eV

VI

$82210 - R/(n - .30)^2$

n		I.P. - ν
(3)	$\tilde{F}$	1.796
(4)		.988
(5)		.612

I.P. = 10.190 eV

In addition to these series, for which specific transitions are listed, Sutcliffe and Walsh also report observing two additional Rydberg series with quantum defect $\delta \approx .90$; and another with quantum defect δ between .75 and .80. The total number of these series then is nine.

The results of model calculations on allene are as follows:

$a_1(ns\sigma_g)$, $\delta = .90$	$a_1(nd\sigma_g)$, $\delta = .20$	$b_2(np\sigma_u)$, $\delta = .53$
3.065	1.730	2.233
1.395	.881	1.097
.798		.660
.506		.437

$e(np\pi_u)$, $\delta = .54$	$e(nd\pi_g)$, $\delta = .26$
2.240	1.822
1.057	1.158
.564	.860

The basis sets used in these calculations were as follows. The hydrogens were neglected, so that calculations were actually performed for a C=C=C, core of symmetry $D_{\infty h}$. The symmetry of the orbitals as calculated are indicated in parentheses above. Gaussian functions were placed at each of the atomic centers and at centers 3.0 a.u. to either side of the atomic centers on the molecular axis. For the $ns\sigma_g$ and $np\sigma_u$ orbital calculations these were:

Center	Exponent	Type
Exterior Carbons	.45	s and p_z
	.15	
	.05	
Center Carbon	.0166	s and p_z
	.0055	
	.0018	
	.0006	
	.0002	

For the $np\pi_u$ orbital calculations they were:

Center	Exponent	Type
Exterior Carbons	.45	p_x
	.15	
	.05	
	.0166	
	.0055	
	.0018	
	.0006	
Center Carbon	.45	p_x
	.15	
	.05	

For the $nd\sigma_g$ orbital calculations they were:

Center	Exponent	Type
Exterior Carbons	.45	p_z
	.15	
	.05	
	.0166	
	.0055	
	.0018	
	.0006	
Center Carbon	.45	p_z
	.15	
	.05	

Finally for the $nd\pi_g$ orbital calculations they were:

Center	Exponent	Type
Exterior Carbons	.45	p_x
	.15	
	.05	
	.0166	
Extended Centers	.0055	p_x
	.0018	
	.0006	
	.0002	

On the basis of the model calculations we can interpret the optical spectrum as follows.

Series I, with the exception of the n = 4 member, fits well with the calculated $a_1(ns\sigma_g)$ series. We assign this series as $^1E(a_1)$. There are two additional series with quantum defect $\delta \approx .90$ reported by Sutcliffe and Walsh and we would assign these as $^1E(a_1)$ also, making all three series vibrational members of essentially the same Rydberg series.

Series II can be fit with either the $b_2(np\sigma_u)$ or the $e(np\pi_u)$ series. The same can be said of series III and IV. However, series II seems to be a single series, and series III and IV to be double. On this basis we assign series II as $^1E(b_2)$ and series III and IV as $^1B_2(e)$. The other reported series with quantum defect δ between .75 and .80 we would then identify as another vibrational member of the $^1E(b_2)$ series, since the quantum defects are comparable, .70 vs. .75.

Both series V and IV fit well with an $a_1(nd\sigma_g)$ or $e(nd\pi_g)$ series. Thus we identify these as $^1E(a_1)$ or $^1B_2(e)$. They may either be vibrational levels of the same series or different series, it is difficult to decide.

Thus, in the case of allene, if we use Herzberg's suggestion that some of the observed Rydberg bands are simply vibrational members of a few basic series, we can account nicely for all of the observed transitions.

References

1. R. J. Buenker, J. Chem. Phys. 48, 1368 (1968).

2. L. H. Sutcliffe and A. D. Walsh, J. Chem. Soc., 899 (1952).

3. G. Herzberg, Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand, New York (1966), p. 542.

4.15 ACETALDEHYDE

The ground state of acetaldehyde $\tilde{X}$ is planar of symmetry C_s, and so presumably are the excited states. Thus the selection rules for dipole allowed transitions from the ground state are:

$^1A'' \leftarrow \tilde{X}$ z transition

$^1A' \leftarrow \tilde{X}$ x, y transition

Infrared, raman and microwave spectroscopy give the following values for the geometry of the ground state $\tilde{X}$:

C–C ~ 2.837 a.u. ∠ CCO ~ 123.9°

C=O ~ 2.298 a.u. ∠ HCH ~ 108.3°

C–H ~ 2.052 a.u. ∠ CCH ~ 117.5°

2.105 a.u.

The orbital energies of acetaldehyde have not been calculated to date, but using formaldehyde as an analogy, we can write the electronic configuration of the ground state $\tilde{X}$ of acetaldehyde as:

$$\{\text{core}\}\ (2a'')^2 - {}^1A''$$

where {core} is made up of filled a′ orbitals, and one filled a″ orbital.

The electronic configuration of the Rydberg states converging to the first ionization limit is then:

$$\{\text{core}\}(2a'')(nR)$$

We see that there are no restrictions on the symmetry of the Rydberg orbitals for dipole allowed transitions.

The optical spectrum of acetaldehyde begins in the region 3500 Å to 2500 Å with a weak absorption to an $\tilde{A}(\{core\}(2a'')(3a'')) \leftarrow \tilde{X}$ (presumably π^* - n) transition. This absorption has been definitely confirmed as due to an excitation in the $\diagdown$C=O$\diagup$ group.[1]

Below 2000 Å there are two prominent band systems at 1818 Å and 1662 Å. Walsh[2] has organized these band systems and other discrete bands in the region into three different Rydberg series, they are:

$82505 - R/(n - .70)^2$

n		I.P. - ν
(3)	$\tilde{C}$	2.768 (at 1662 Å)
(4)		1.258
(5)		.733
(6)		.481

I.P. = 10.226 eV

$82475 - R/(n - .20)^2$

n		I.P. - ν
(3)	$\tilde{E}$	1.790
(4)		.958
(5)		.590
(6)		.404

I.P. = 10.222 eV

$82504 - R/(n - .90)^2$

n		I.P. - ν
(3)	$\tilde{B}$	3.410 (at 1818 Å)
(4)		1.416
(5)		.806
(6)		.520

I.P. = 10.226 eV

The first series above is easily observed in the spectrum and provides one of the longest Rydberg series thus far observed in a polyatomic molecule.

Model calculations on acetaldehyde give the following results.

a′, δ = .96	a′, δ = .91	a′, δ = .34
3.275	3.120	1.919
1.416		
.807		
.505		

a″, δ = .63	a″, δ = .08
2.433	1.589
1.203	

The basis sets used in these calculations are as follows. The hydrogens were neglected to simplify the calculations to those for a bent C_2O core. Gaussian basis functions were placed at each of the atomic centers and at the center of gravity of the C_2O core, corresponding to each atom having unit mass. For the a′ orbital calculations these functions were:

Center	Exponent	Type
Carbons	.45	s
Oxygen	.45	s

Center	Exponent	Type
Center of Gravity	.45	s, p_x and p_z
	.15	
	.05	
	.0166	
	.0055	
	.0018	
	.0006	

For the a″ orbital calculations they were:

Carbons, Oxygen	.45	p_y
	.15	
	.05	
	.0166	
	.0055	

The interpretation of the optical spectra proceeds as follows. The first series with quantum defect $\delta = .70$ fits well with the calculated a″ series with $\delta = .63$. We would interpret these orbitals as 'p' like orbitals out of the plane of the molecule. These states are thus $^1A'(a'')$ states.

The second Rydberg series is ambiguous, it could conceivably fit either with the a′, $\delta = .34$ or a″, $\delta = .08$ series, or possibly even another series not calculated here. Because of the difficulties with our calculations we can not assign this series.

The third series fits well with the a′, $\delta = .96$ series. We exclude the possibility of a fit with the a′, $\delta = .91$ series because of

the excellent agreement of the 2nd, 3rd, and presumably higher members of the calculated and experimental series and because we expect[3] the occurrence of an 's' like Rydberg series. We assign these states then as $^1A''(a')$.

We can, therefore, identify two of the three known Rydberg series in acetaldehyde as due to transitions from 'ns' and 'np' Rydberg orbitals. If we use the analogy of acetaldehyde and formaldehyde we would expect that the unassigned series is a 'nd' series, and that it is probably described by the a", $\delta = .08$ series above.

REFERENCES

1. G. Herzberg, Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand, New York (1966), p. 542.

2. A. D. Walsh, Proc. Roy. Soc., 185A, 176 (1946).

3. G. Herzberg, Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand, New York (1966), p. 544.

4.16 PROPYNE (METHYL ACETYLENE)

The ground state of propyne $\tilde{X}$ is of symmetry C_{3v}, and in the absence of any evidence to the contrary we shall assume that this is true of the excited states also. Thus, the selection rules for dipole allowed transitions to the ground state are:

$$^1A_1 \leftarrow \tilde{X} \qquad \text{z transition}$$

$$^1E_1 \leftarrow \tilde{X} \qquad \text{x, y transition}$$

Infrared, raman, and microwave spectroscopy yield the following geometrical parameters for the ground state $\tilde{X}$:

$C \equiv C \sim 2.757$ a.u. $\qquad C-H \sim \begin{cases} 2.088 \text{ a.u.} \\ 1.996 \text{ a.u.} \end{cases}$

$C-C \sim 2.279$ a.u. $\qquad \angle HCH \sim 110.2^\circ$

As yet no one has calculated the orbital energies for propyne. However, it is easy to write the electronic configuration of the molecule because of the simplicity of the group C_{3v}.

In this group an orbital may transform as either the representation a_1, a_2 or e. Obviously the π bonds transform as e; hence, in analogy with acetylene, we may write the electronic configuration of the ground state $\tilde{X}$ as:

$$\{\text{core}\}\,(1e)^4 \; - \; ^1A_1$$

where {core} represents the orbitals corresponding to the core orbitals of acetylene, with the hydrogen atoms replaced by methyl groups.

The electronic configuration of the lowest Rydberg series will be:

$$\{\text{core}\}\ (1e)^3(nR)$$

We see that there are no symmetry restrictions on the Rydberg orbital in order that a transition be dipole allowed.

Propyne begins to absorb at about 2000 Å. From 2000 Å to 1880 Å there is a broad continuum with a maximum at 1920 Å which has been assigned to the transition $\tilde{A}(\{\text{core}\}(1e)^3(2e)?) \leftarrow \tilde{X}$. From 1750 Å to 1600 Å there is another continuum with maximum at 1650 Å, assigned to the transition $B(\{\text{core}\}(1e)^2(2e)^2?) \leftarrow \tilde{X}$. Both of these continua contain diffuse bands, and may indeed be made up of a superposition of many diffuse bands.

At shorter wavelengths observers have assigned Rydberg series converging to two different ionization limits.

Nakayama and Watanabe[1] observed three Rydberg series converging to an ionization limit of 83590 cm^{-1} or 10.361 eV. They are:

R		R′	
$83570 - R/(n - .98)^2$		$83580 - R/(n - .57)^2$	
n	I.P. − ν	n	I.P. − ν
(4) $\tilde{F}$	1.529	(3) $\tilde{D}$	2.314
(5)	.841	(4)	1.151
(6)	.539	(5)	.697
I.P. = 10.358 eV		I.P. = 10.359 eV	

R″

$$83600 - R/(n - .33)^2$$

n		I. P. - ν
(3)	$\tilde{E}$	1.916
(4)		1.004
(5)		.619

I. P. = 10.362 eV

The value of the ionization limit alone agrees with the value for the first ionization potential deduced from electron impact and photo-ionization measurements.[2]

Earlier than this, Price and Walsh[3] observed two Rydberg series converging to separate ionization limits of 91100 and 91240 cm^{-1} or 11.292 eV and 11.310 eV. These series are:

$$91240 - R/(n - .52)^2$$

n		I. P. - ν
(3)	$\tilde{G}$	2.187
(4)		1.116
(5)		.680
(6)		.452

I. P. = 11.310 eV

$$91100 - R/(n - .96)^2$$

n		I. P. - ν
(3)	$\tilde{C}$	3.246
(4)		1.472
(5)		.833
(6)		.534

I. P. = 11.292 eV

These series could not be confirmed by Nakayama and Watanabe since the region below 1200 Å where most of the members of the series were measured, was composed of almost continuous absorption in their instrument. Furthermore, the first member of their R′ series is the same as the first member of the second of Price and Walsh's series.

There is some doubt as to the existence of at least one of these series, but the possibility of their existence is not completely discounted by Herzberg.[2]

The result of model calculations on propyne are as follows:

$a_1(ns\sigma)$, $\delta = .90$	$a_1(np\sigma)$, $\delta = .53$	$a_1(nd\sigma)$, $\delta = .54$
3.095	2.229	2.256
1.421	1.096	1.182
.817	.660	.685
.515	.437	

$e(np\pi)$, $\delta = .62$	$e(nd\pi)$, $\delta = .59$
2.380	2.344
1.330	1.181
.724	.467
.417	

The following basis sets were used. For the purpose of calculation the hydrogens were neglected leaving a linear C–C≡C core. The symmetries in parenthesis above are the symmetries of the orbitals as calculated for this $C_{\infty\nu}$ core. Gaussian functions were placed at each of the atomic centers. For the nsσ and npσ orbital calculations these functions were:

Center	Exponent	Type
End Carbons	.45	s and p_z
	.15	
	.05	

Center	Exponent	Type
Center Carbon	.0166	s and p_z
	.0055	
	.0018	
	.0006	
	.0002	

For the npπ and ndπ orbital calculations they were:

Center	Exponent	Type
End Carbons	.45	p_x
	.15	
	.05	
	.0166	
	.0055	
	.0018	
	.0006	
Center Carbon	.45	p_x
	.15	
	.05	

Finally, for the ndσ orbital calculations they were:

Center	Exponent	Type
End Carbons	.45	p_z
	.15	
	.05	
	.0166	
	.0055	
	.0018	
	.0006	
Center Carbon	.45	p_z
	.15	
	.05	

In analogy with acetylene, we assign the R and R′ series of Nakayama and Watanabe as $a_1(ns\sigma)$ and $e(nd\pi)$ respectively, considering the presence of the methyl group to be a minor perturbation on the acetylenic spectrum. The states corresponding to these series are then $^1E(a_1)$ and $^1A_1(e)$ respectively.

That the R series is an $ns\sigma$ series is manifest. The missing n = 3 member at 56,600 cm^{-1} is probably one of the diffuse bands buried in the $\tilde{B}$ continuum.

The other assignment is made purely on the expected resemblance of the acetylene and propyne spectra, since all of the remaining calculated orbitals can be fit with this series.

The R″ series is something of a mystery. It does not fit with any of our series. By exclusion, one might assign it as $e(nd\delta)$ and the states as $^1A_1(e)$.

As for Price and Walsh series, without questioning their reality, we can assign them as $e(nd\pi)$ and $a_1(ns\sigma)$ just like the R′ and R series.

That these states might really imply the existence of a low lying excited state ion of $CH_3C_2H^+$ has been discussed by Herzberg.[2]

REFERENCES

1. T. Nakayama and K. Watanabe, J. Chem. Phys. 40, 558 (1964).

2. G. Herzberg, Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand, New York (1966), p. 542.

3. W. C. Price and A. D. Walsh, Trans. Far. Soc. 41, 381 (1945).

4.17 ACROLEIN

Like 1,3 butadiene, acrolein can twist about a carbon-carbon single bond to take trans and cis forms. However, unlike 1,3 butadiene where both trans and cis forms exist in appreciable concentrations at room temperature, in acrolein the trans form appears almost exclusively. This is proved by the existence of k structure of a nearly symmetric top in the perpendicular bands of the acrolein spectra under high resolution.[1]

With the form of the acrolein molecule thus established, we see that the dipole allowed transitions from the ground state $\tilde{X}$ (symmetry C_{1h}) will be:

$^1A'' \leftarrow \tilde{X}$	z transition
$^1A' \leftarrow \tilde{X}$	x, y transition

Microwave, infrared and raman spectroscopy applied to acrolein have yielded the following geometrical parameters for the ground state $\tilde{X}$:

C–C ~ 2.74 a.u.	∠ CCC ~ 122°
C=C ~ 2.57 a.u.	∠ CCO ~ 125°
C=O ~ 2.31 a.u.	

To date there have been no orbital energies calculated for acrolein, but we can get an idea of the electronic configuration for acrolein from the known results on trans-butadiene. We expect the

electronic configuration for acrolein to be:

$$\{\text{core}\}(2a'')^2 - {}^1A'$$

where the orbital (2a″) is the analogue of the orbital ($1b_g$) in trans-butadiene. Similarly the {core} part is the analogue of $\{\text{core}\}_T$ in trans-butadiene in which one of the end carbons has been replaced by an oxygen atom.

From this, we see that the electronic configuration of the Rydberg states converging to the first ionization limit is:

$$\{\text{core}\}(2a'')(nR)$$

and the dipole allowed transitions will be ${}^1A''(a')$ and ${}^1A'(a'')$.

The optical spectrum of acrolein shows a weak absorption in the region 3870 Å to 3000 Å (maximum at 3300 Å), which has been assigned to the transition $\tilde{A}(\{\text{core}\}(2a'')(3a'')) \leftarrow \tilde{X}$. This transition is described as a π^*-n transition localized about the C=O bond.

A very weak absorption, assigned as $\tilde{a}(\{\text{core}\}(2a'')(3a'')) \leftarrow \tilde{X}$, corresponding to the triplet version of the above transition can be seen in a series of bands at 4122 Å.

Another, much stronger absorption starts at 2350 Å. This transition, assigned as $\tilde{B}(\{\text{core}\}(2a'')(4a'')) \leftarrow \tilde{X}$ corresponds to a $\pi^* \leftarrow \pi$ transition, this time localized about the C=C bond.

At shorter wavelengths, Walsh[2] has found three Rydberg series converging to an ion formed by the removal of the lone-pair electron of the oxygen atom. They are:

$81500 - R/(n - .15)^2$		$81460 - R/(n - .95)^2$		$81516 - R/(n - .68)^2$	
n	I.P. - ν	n	I.P. - ν	n	I.P. - ν
(3) $\tilde{F}$	1.734	(4) $\tilde{G}$	1.605	(3) $\tilde{D}$	2.595
(4)	.935	(5)	.800	(4)	1.243
(5)	.588	(6)	obscured	(5)	.727
I.P. = 10.102 eV		I.P. = 10.097 eV		(6)	.481
				I.P. = 10.104 eV	

In addition to these series, there are two bands $\tilde{C}$ and $\tilde{E}$ at 57140 cm^{-1} (7.082 eV) and 62500 cm^{-1} (7.747 eV), respectively, which do not belong to the above series and may represent the beginning of a new Rydberg series converging to the ion formed by removing a π electron from the C=C bond.

The results of model calculations on trans-acrolein are as follows:

Set I

$a'(ns)$, $\delta = .87$	$a'(nd\sigma)$, $\delta = .52$	$a'(np)$, $\delta = .52$
2.984	2.211	2.214
1.377	1.127	1.090
.792	.666	.656
.501	.451	.435

$a'(np), \delta = .52$	$a''(np), \delta = .58$	$a''(nd), \delta = .02$
2.189	2.316	1.527
1.124	1.161	.848
.696	.714	
.456		

Set II

$a'(ns), \delta = 1.00$	$a'(nd\sigma), \delta = .64$	$a'(np), \delta = .35$
3.413	2.543	1.927
1.507	1.207	.993
.841	.652	.604
.513	.446	.415

$a'(np), \delta = .66$	$a''(np), \delta = .69$	$a''(nd), \delta = -.07$
2.484	2.537	1.444
1.222	1.233	.811
.733	.727	
.469		

The first set of calculations corresponds to the charge distributed evenly on the atoms as is usual for these calculations. In the second set, the total charge has been divided equally between the oxygen and carbon atoms forming a double bond. This has been done to bring out the effect of the C=O group on the spectrum. We expect that this approach is valid because of the pronounced

similarity of the acrolein spectrum with the acetaldehyde spectrum, which contains a C=O group, but not a C=C group.

The basis sets used in these calculations were as follows. The hydrogen atoms were neglected leaving a C_3O core, thus simplifying calculations. A z axis was constructed passing through the midpoints of the carbon-carbon and carbon-oxygen double bonds; and the x axis was taken at right angles to this in the plane of the molecule. Gaussian functions were placed at centers located at the atomic centers and at the origin of the coordinate system. For the a'(ns) and a'(np) orbital calculations these functions were:

Center	Exponent	Type
Oxygen }	.45	s and p_z
End Carbon }	.15	
Origin	.45	s and p_z
	.15	
	.05	
	.0166	
	.0055	
	.0018	
	.0006	

For the other a'(np) orbital these functions were:

Center	Exponent	Type
Oxygen, End Carbon	.0166	p_x
	.0055	
	.0018	
	.0006	
Center Carbons	.45	p_x
	.15	
	.05	

For the a″(np) and a″(nd) orbital calculations they were:

Center	Exponent	Type
Oxygen, End Carbon	.45	p_y
	.15	
	.05	
	.0166	
	.0055	
	.0018	
Center Carbons	.45	p_y
	.15	
	.05	

Finally for the a′ (ndσ) orbital calculations they were:

Center	Exponent	Type
Oxygen	.0166	p_z
End Carbon	.0055	
	.0018	
	.0006	
Center Carbons	.45	p_z
	.15	
	.05	

When we come to interpret the acrolein spectrum we get results very similar to those for acetaldehyde.

We interpret the series with quantum defect $\delta = .95$ as an ns series, the experimental quantum defect lying between as it were the results of the set I and II calculations. These states are then $^1A''(a')$ Rydberg states. The only problem connected with this series is the whereabouts of the $n = 3$ member. It is expected at about 54,000 cm^{-1}, which lies within the $\tilde{B}$ continuum (42,500 cm^{-1} - 55,500 cm^{-1}).

Likewise the series with quantum defect $\delta = .68$ lies between the set I and II results for the a"(np) series. We interpret these states as $^1A'(a'')$ states. It would seem possible to also fit this series with an a'(np) series or even an a'(ndσ) series.

However, we do not do this. In explaining why we first note that the set II calculations show a better agreement with experiment than the set I results. This suggests that the transitions with which we deal are highly localized on the C=O double bonds. The a"(np)

series assigned above is consistent with the usual interpretation of an excitation out of the lone pair electrons on the oxygen atom, which our results show is a good description of the system. Thus we prefer this assignment on chemical grounds as well as on the grounds that it is best fit to the experimental result.

The last series with quantum defect $\delta = .15$ is a bit troublesome. It does not fit well with any of our calculated series. The analogous series in acetaldehyde shows the same behavior. The series is probably an a″(nd) series despite the poor agreement with our calculations.

Finally, we note that the band $\tilde{E}$, which has been suggested as being a member of a series converging to the second ionization limit of acrolein, fits reasonably well with an a′(3p) or even an a′(3dσ) band converging to the first ionization limit.

REFERENCES

1. G. Herzberg, Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand, New York (1966), p. 547.

2. A. D. Walsh, Trans. Far. Soc., 41, 498 (1945).

4.18 DIMETHYL ETHER

The ground state of dimethyl ether $\tilde{X}$ is of symmetry C_{2v} and we shall assume that the same is true of its excited states. Thus the selection rules for dipole allowed transitions from the ground state are:

$^1B_1 \leftarrow \tilde{X}$	x transition
$^1B_2 \leftarrow \tilde{X}$	y transition
$^1A_1 \leftarrow \tilde{X}$	z transition

Infrared, raman and microwave measurements made on the ground state $\tilde{X}$ give the following geometrical parameters for this state:

C–O ~ 2.665 a.u.	$\angle$COC ~ 111.7°
C–H ~ 2.071 a.u. (ave.)	$\angle$HCH ~ 109.5° (ave.)

To date, no calculations have been performed on dimethyl ether. However, we can get an approximate idea of the orbital scheme for this molecule.

We recognize that the highest orbital will correspond roughly to the out of plane P atomic orbital on the oxygen atom. This orbital has symmetry b_2, and is the only orbital with this symmetry in the ground state, thus the electronic configuration of the ground state can be written as:

$$\{\text{core}\}\ (1b_2)^2 - {}^1A_1$$

Similarly, the electronic configuration of the Rydberg states converging to the first ionization limit will be:

$$\{\text{core}\}\ (1b_2)\ (nR)$$

and the dipole allowed transitions are $^1B_1\ (a_2)$ $^1B_2(a_1)$ and $^1A_1\ (b_2)$; where the symmetry in parenthesis is the symmetry of the Rydberg orbital.

The optical spectrum of dimethyl ether begins with a weak continuous absorption starting at about 2350 Å. This has been attributed to a transition $\tilde{A}$ ($\{\text{core}\}\ (1b_2)\ (?)$) $\leftarrow \tilde{X}$. Starting at about 1880 Å this continuum is replaced by a progression of diffuse bands of which some of the higher members have been arranged into a Rydberg series by Hernandez.[1] This Rydberg series has the formula:

$$80330 - R/(n - .02)^2$$

n		I.P. - ν
(3)	$\tilde{E}$	1.514
(4)		.867
(5)		.553

I.P. = 9.957 eV

The other diffuse bands which have been observed are as follows:

Band	I.P. - ν
$\tilde{F}$	1.135
$\tilde{D}$	2.348
$\tilde{C}$	2.666
$\tilde{B}$	3.370

We have listed these bands together with the Rydberg series because it seems probable that some of these bands can be fit into series also.

The results of model calculations on dimethyl ether are as follows:

$a_1(ns)$, $\delta = .91$	$a_1(np)$, $\delta = .62$	$b_1(np)$, $\delta = .52$
3.084	2.397	2.224
1.404	1.170	1.093
.802	.695	.657
.503	.446	.435

$b_2(np)$, $\delta = .64$	$a_2(nd)$, $\delta = .08$
2.435	1.588
1.206	

The basis sets used were as follows. The hydrogen atoms were neglected, reducing the calculation to one for a C_2O, C_{2v} core. Gaussian functions were placed at the atomic centers and at the center of gravity of the molecule, each atom considered as having unit mass. For the a_1 and b_1 orbital calculations these functions were:

Center	Exponent	Type
Carbons	.45	s
Oxygen	.45	s
Center of Gravity	.45	s, p_x and p_z
	.15	
	.05	
	.0166	

Center	Exponent	Type
	.0055	
	.0018	
	.0006	

For the a_2 and b_2 orbital calculations they were:

Center	Exponent	Type
Carbons, Oxygen	.45	p_y
	.15	
	.05	
	.0166	
	.0055	

The interpretation of the optical spectrum is fairly straightforward. Hernandez's series with quantum defect $\delta = .02$ is obviously either an $a_1(ns)$ or an $a_2(nd)$ series. We prefer the first interpretation as it allows us to renumber the series, making $\delta = 1.02$, and to identify the first member of the series with the previously unassigned band $\tilde{B}$.

The two bands $\tilde{D}$ and $\tilde{F}$ look like the first two members of an 'np' Rydberg series, either an $a_1(np)$ or a $b_2(np)$ series, since the $b_1(np)$ series is dipole forbidden. The fit is actually best with the $a_1(np)$ series, although the $b_2(np)$ possibility cannot be completely excluded.

If we accept the above $a_1(np)$ assignment, then the $\tilde{C}$ band might be the first member of the other 'np' series, i.e., $b_2(3p)$. However, the agreement between the calculated and experimental values is a bit poor to insist on this assignment.

Thus, all of the observed bands can be plausibly accounted for by our calculations.

REFERENCES

(1) G. J. Hernandez, J. Chem. Phys., 38, 1644 (1963).

4.19 1,3-BUTADIENE

Since 1,3-butadiene contains two carbon-carbon double bonds, linked together by a carbon-carbon single bond, the molecule is free to rotate about this latter single bond, and assume trans and cis forms. It has been determined,[1] mainly from calorimetric data that at room temperature the predominant form is trans, but that the cis exists in appreciable quantities (approximately 4% of the total molecules are cis).

If we assume that the excited states have the same symmetries as the ground states (C_{2h} for the trans form, C_{2v} for the cis), then the selection rules for the dipole allowed transitions from the ground state are for trans-butadiene:

$^1A_u \leftarrow \tilde{X}$	z transition
$^1B_u \leftarrow \tilde{X}$	x, y transition

and for cis-butadiene they are:

$^1B_1 \leftarrow \tilde{X}$	x transition
$^1B_2 \leftarrow \tilde{X}$	y transition
$^1A_1 \leftarrow \tilde{X}$	z transition

Infrared, raman spectroscopy and electron diffraction have been applied to determining the interatomic parameters of the ground state of 1,3 butadiene. The results which they give are:

C–C ~ 2.789 a.u. $\angle$CCC ~ 122.9°

C=C ~ 2.526 a.u.

The orbital energies for both trans and cis butadiene have been calculated by Buenker and Whitten.[2] Their results can be summarized by the following table:

trans-butadiene		cis-butadiene	
$1a_g$	-11.347	$1a_1$	-11.346
$1b_u$	-11.346	$1b_2$	-11.346
$2b_u$	-11.310	$2b_2$	-11.305
$2a_g$	-11.310	$2a_1$	-11.304
$3a_g$	- 1.109	$3a_1$	- 1.115
$3b_u$	- 1.021	$3b_2$	- 1.011
$4a_g$	- 0.838	$4a_1$	- 0.857
$4b_u$	- 0.775	$4b_2$	- 0.744
$5a_g$	- 0.664	$5a_1$	- 0.707
$5b_u$	- 0.660	$6a_1$	- 0.629
$6a_g$	- 0.574	$5b_2$	- 0.602
$6b_u$	- 0.569	$6b_2$	- 0.537
$7a_g$	- 0.514	$7a_1$	- 0.526
$1a_u$	- 0.477	$1b_1$	- 0.477
$1b_g$	- 0.358	$1a_2$	- 0.354
E_T	-154.7103	E_T	-154.7023

Thus the electronic configuration of trans-butadiene is:

$$\{\text{core}\}_T(1b_g)^2 - {}^1A_g$$

where $\{\text{core}\}_T$ consists of the orbitals:

$$(1a_g)^2(1b_u)^2(2b_u)^2(2a_g)^2(3a_g)^2(3b_u)^2(4a_g)^2(4b_u)^2(5a_g)^2(5b_u)^2 \times (6a_g)^2(6b_u)^2(7a_g)^2(1a_u)^2$$

and the electronic configuration of cis-butadiene is:

$$\{\text{core}\}_c(1a_2)^2 - {}^1A_1$$

where $\{\text{core}\}_c$ is comprised of the orbitals:

$$(1a_1)^2(1b_2)^2(2b_2)^2(2a_1)^2(3a_1)^2(3b_2)^2(4a_1)^2(4b_2)^2(5a_1)^2(6a_1)^2(5b_2)^2 \times (6b_2)^2(7a_1)^2(1b_1)^2$$

Using the above results we see that the electronic configuration of the Rydberg states converging to the first ionization limit of trans-butadiene will be:

$$\{\text{core}\}_T\ (1b_g)(nR)$$

and we see that the dipole allowed transitions are ${}^1A_u(b_u)$ and ${}^1B_u(a_u)$, where the symmetries in parenthesis are the symmetries of the Rydberg orbitals.

The electronic configuration of the Rydberg states converging to the first ionization limit of cis-butadiene will be:

$$\{\text{core}\}_c(1a_2)(nR)$$

and the dipole allowed transitions are then

$$^1B_1(b_2),\ ^1B_2(b_1) \text{ and } ^1A_1(a_2).$$

The optical spectrum of 1, 3 butadiene begins with a progression of diffuse bands between 2170 Å and 1970 Å. The transition involved is thought to be analogous to the $\pi^* \leftarrow \pi$ transition in ethylene and is designated $\tilde{A}(\{\text{core}\}_T(1b_g)(2a_u)) \leftarrow \tilde{X}$.

The above bands are followed by a number of strong single and double bands on the region 2000 - 1600 Å, which apparently represent single electronic transitions.

Below 1520 Å a number of sharp bands are observed which have been put into two Rydberg series by Price and Walsh.[3] They are:

$73115 - R/(n - .10)^2$			$73066 - R/(n - .50)^2$		
n		I.P. - ν	n		I.P. - ν
(3)		1.611	(4)	$\tilde{G}$	1.062
(4)	$\tilde{H}$	.894	(5)		.675
(5)		.563	(6)		.450
I.P. = 9.062 eV			I.P. = 9.056 eV		

The above bands are presumably due to <u>trans</u> butadiene, the predominant species at room temperature. In addition to these series Sugden and Walsh[4] claimed to have observed another series which they attribute to the <u>cis</u> species. It is:

$$70606 - R/(n - .10)^2$$

n	I.P. - ν
(3)	1.587
(4)	.896
(5)	obscured by 1515 Å doublet

I.P. = 8.751 eV

This series is not confirmed by Herzberg[5], however.

In addition to these series, we want to consider some of the bands in the 2000 - 1600 Å region which we may be able to assign. They are:

Band	9.06 - ν	8.75 - ν
$\tilde{F}$	1.997	1.687
$\tilde{E}$ (diffuse)	2.018	1.708
$\tilde{D}$	2.248	1.939
$\tilde{C}$	2.405	2.095
$\tilde{B}$	2.801	2.491

All of these bands are strong and sharp with the exception of $\tilde{E}$. We have subtracted them from both of the experimental ionization potentials because we want to consider the possibility of both trans and cis transitions.

The results of model calculations on trans butadiene are as follows:

$a_g(ns)$, δ=.76	$a_g(nd\sigma)$, δ=.22	b_u, δ = .42
2.714	1.761	2.039
1.327	.993	1.045
.772	.631	.635
.495		.429

b_u, δ = .38	$a_u(np)$, δ = .47
1.970	2.119
1.109	1.091
.656	.782

and for cis-butadiene they are:

$a_1(ns)$, δ = .78	$a_1(np\sigma)$, δ = .52	$b_2(np\pi)$, δ = .46	$b_1(np\pi)$, δ = .68
2.748	2.202	2.098	2.321
1.291	1.098	1.044	1.149
.751	.662	.630	.688
.488	.437	.426	.444

The basis sets used in these calculations were as follows. First the hydrogens were neglected, reducing the calculation to one for a C_4 core.

For trans butadiene a z axis was constructed passing through the midpoints of the two carbon-carbon double bands, and the x axis was taken at right angles to this in the plane of the molecule. Gaussian functions were placed at centers located at the atomic

centers and at the midpoint of the C_4 core. For the $a_g(ns)$ and b_u orbital calculations these functions were:

Center	Exponent	Type
End Carbons	.45	s and p_z
	.15	
Midpoint	.45	s and pz
	.15	
	.05	
	.0166	
	.0055	
	.0018	
	.0006	

For the other b_u orbital, these functions were:

Center	Exponent	Type
End Carbons	.0166	p_x
	.0055	
	.0018	
	.0006	
Center Carbons	.45	p_x
	.15	
	.05	

For the $a_u(np\pi)$ orbital calculations these functions were:

Center	Exponent	Type
End Carbons	.45	p_y
	.15	
	.05	
	.0166	
	.0055	
	.0018	
Center Carbons	.45	p_y
	.15	
	.05	

Finally, for the $a_g(nd\sigma)$ orbital the functions were:

Center	Exponent	Type
End Carbons	.0166	p_z
	.0055	
	.0018	
	.0006	
Center Carbons	.45	p_z
	.15	
	.05	

For the cis-butadiene calculations Gaussian functions were placed at each of the atomic centers, and at the center of gravity of the molecule. For the $a_1(ns)$, $a_1(np\sigma)$ and $b_2(np\pi)$ orbital calculations these functions were:

Center	Exponent	Type
Carbons	.45	s
Center of Gravity	.45	s, p_x and p_z
	.15	
	.05	
	.0166	
	.0055	
	.0018	
	.0006	

Finally, for the $b_1(np\pi)$ orbital calculations these functions were:

Center	Exponent	Type
Carbons	.45	p_y
	.15	
Center of Gravity	.05	p_y
	.0166	
	.0055	
	.0018	
	.0006	

We can only interpret part of the optical spectrum on the basis of our calculations. We interpret the Price and Walsh Rydberg series with $\delta = .50$ as a np series, the best fit being with the first b_u series, making the states $^1A_1$ states. Furthermore, we suggest that the missing n = 3 member of this series is the $\tilde{F}$ band which lies 1.997 eV below the trans ionization limit.

The other Price and Walsh series with quantum defect $\delta = .10$ does not fit with either the ns or the dipole allowed np series. The experimental spectrum is described as strong. This suggests that in this state the molecule is distorted from C_{2h} symmetry, and that the series is a dipole forbidden nd series which acquires intensity through this distortion.

We now examine the bands in the 2000 - 1600 Å region. We have already assigned one band in this region (i.e. $\tilde{F}$); and we note that the $\tilde{D}$ band would fit well with the first member of an a_u(np) series. Similarly, the $\tilde{E}$ band, although diffuse could conceivably be a first member of the other dipole allowed b_u series. We already know that there are bands near where the second and higher members of these proposed series should be, so we may speculate that the concurrence of so many bands has made the identification of the separate series impossible until now. Thus we assign the $\tilde{D}$ and $\tilde{E}$ bands as $^1B_u(a_u)$ and $^1A_u(b_u)$ respectively.

Let us consider Sugden and Walsh's series, with quantum defect $\delta = .10$. The dipole allowed orbitals are a_2, b_1 and b_2. While we have only calculated the latter two types of orbitals, it is clear that neither of them can account for Sugden and Walsh's series. Thus by implication, the series is probably an a_2(nd) series, and the states are $^1A_1(a_2)$ states.

We suspect that the nd Rydberg orbital of Sugden and Walsh's series is identical to the nd Rydberg orbital of the similar Price and Walsh series; and that as soon as the molecule is distorted from C_{2h} symmetry the transition attains considerable intensity.

We get more indirect confirmation of the correctness of Sugden and Walsh's assignment when we consider the unassigned bands in the region 2000-1600 Å. Comparing our results with the experimental term values subtracted from their proposed cis-butadiene ionization potential, we see that the $\tilde{C}$ band looks like the first member of a $b_2(np\pi)$ series and the $\tilde{B}$ band is consistent with the first member of a $b_1(np\pi)$ series. As noted above, Herzberg is a bit skeptical about the existence of a cis-butadiene series, and the value of the cis-butadiene ionization potential. Our results show that the existence of a cis-butadiene spectrum and an ionization limit of approximately 8.7 eV for cis-butadiene can account not only for Sugden and Walsh's series, but two unassigned bands as well. We then assign the $\tilde{C}$ and $\tilde{B}$ bands as $^1B_1(b_2)$ and $^1B_2(b_1)$, respectively.

REFERENCES

1. J. G. Aston, G. Szasz, H. W. Woolley, F. G. Brickwedde, J. Chem. Phys., 14, 67 (1946).
2. R. J. Buenker, J. L. Whitten, J. Chem. Phys., 49, 5381, (1968).
3. W. C. Price, A. D. Walsh, Proc. Roy. Soc., 174A, 220 (1940).
4. T. M. Sugden, A. D. Walsh, Trans. Far. Soc., 41, 76 (1945).
5. G. Herzberg, Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand, New York (1966), p. 550.

4.20 2-BUTENE

The most outstanding fact about 2-butene is that it exists in two different geometrical isomer forms, namely trans-butene-2 and cis-butene-2. These have symmetries C_{2h} and C_{2v} respectively. Thus if we assume that the excited states have the same symmetries as the ground states the selection rules for the dipole allowed transitions from ground state are for trans-butene:

$^1A_u \leftarrow \tilde{X}$	z transition
$^1B_u \leftarrow \tilde{X}$	x, y transition

and for cis-butene:

$^1B_1 \leftarrow \tilde{X}$	x transition
$^1B_2 \leftarrow \tilde{X}$	y transition
$^1A_1 \leftarrow \tilde{X}$	z transition

The interatomic parameters for both trans and cis butene have been determined by electron diffraction.[1] For trans-butene they are:

C=C ~ 2.64 a.u. $\quad\quad$ ∠ CCC ~ 125°

C–C ~ 2.95 a.u.

and for cis-butene they are:

C=C ~ 2.61 a.u. $\quad\quad$ ∠ CCC ~ 125°

C–C ~ 2.81 a.u.

The hydrogen bond distances and angles are not listed here because they cannot be determined accurately by electron diffraction, and because they are not necessary for our calculations.

No calculations where orbital energies are reported have been published for trans and cis-butene to date, however, we do have some idea of the electronic configurations to be expected for these molecules. We expect the electronic configuration of trans-butene to be:

$$\{\text{core}\}_T(1a_u)^2 - {}^1A_g$$

in analogy with ethylene. The orbital $(1a_u)$ is the analogue of the $(1b_{3u})$ orbital in ethylene. The $\{\text{core}\}_T$ part is similar to the $\{\text{core}\}$ for ethylene, except that two trans-hydrogens are replaced by methyl groups.

Similarly, we expect the electronic configuration of cis-butene to be:

$$\{\text{core}\}_c(1b_1)^2 - {}^1A_1$$

Here, the orbital $(1b_1)$ is analogous to the $(1b_{3u})$ orbital of ethylene, and the $\{\text{core}\}_c$ part is similar to the $\{\text{core}\}$ for ethylene, except that two cis-hydrogens are replaced by methyl groups.

We can then write the electronic configuration of the Rydberg states converging to the first ionization limit of trans-butene as:

$$\{\text{core}\}_T(1a_u)(nR)$$

and we see that the dipole allowed transitions from ground state are ${}^1A_u(a_g)$ and ${}^1B_u(b_g)$, where the symmetries in parenthesis are the

symmetries of the Rydberg orbitals.

Similarly for cis-butene the electronic configuration of the Rydberg states converging to the first ionization limit are predicted to be:

$$\{\text{core}\}_c(1b_1)(nR)$$

and the dipole allowed transitions are $^1B_1(a_1)$, $^1B_2(a_2)$ and $^1A_1(b_1)$.

The optical spectra of both trans and cis- butene begin at about 2100 Å with a continuum. Since these molecules are substituted ethylenes it is not surprising that their spectra should resemble that of ethylene. The first absorption in both is assigned to the V ← N ($\pi^* \leftarrow \pi$) transition which is so prominent in the ethylene spectrum.

Again, both molecules show another absorption at about 49000 cm^{-1} slightly to the red side of the diffuse V ← N transition. This is the so called 'mystery band' which has stirred up so much controversy over the interpretation of the ethylene and related spectra.

McDiarmid[1] has arranged the mystery band and other bands of the trans-butene spectra into two Rydberg series:

$73900 - R/(n - .88)^2$		$74000 - R/(n - .24)^2$	
n	I.P. - ν	n	I.P. - ν
(3)	3.035 (Mystery Band)	(3)	1.756
(4)	1.356	(4)	.995
(5)	.835	(5)	.633
(6)	.550	(6)	.442
I.P. = 9.160 eV		I.P. = 9.172 eV	

For cis-butene she has arranged the mystery band and other bands into the Rydberg series:

$$73550 - R/(n - 1.03)^2$$

n	I.P. - ν	
(3)	3.129	(Mystery Band)
(4)	1.555	
(5)	.854	
(6)	.563	

I.P. = 9.116 eV

The results of model calculations on trans-butene are as follows:

Set I

$a_g(ns\sigma)$, $\delta = .81$	$a_g(nd\sigma)$, $\delta = .31$	b_u, $\delta = .44$
2.821	1.882	2.084
1.340	1.033	1.040
.778	.479	.629
.497		.426

b_u, $\delta = .64$	$a_u(np\pi)$, $\delta = .54$
2.426	2.242
1.236	1.136
.806	.704
.587	

Set II

$a_g(ns\sigma)$, $\delta = .87$	$a_g(nd\sigma)$, $\delta = .31$	b_u, $\delta = .42$	b_u, $\delta = .53$
2.989	1.865	2.040	2.228
1.389	.958	1.033	1.115
.798	.603	.627	.696
.503	.438	.425	.455

Set I corresponds to the results obtained with the charge distributed equally on all atoms (except the hydrogens which are neglected) which is the usual procedure in these calculations. In set II the total charge has been divided equally between the two doubly bonded carbons. This emphasizes the fact that trans-butene is a methyl substituted ethylene.

Similar results are obtained for cis-butene.

Set I

$a_1(ns\sigma)$, $\delta=.76$	$a_1(np\sigma)$, $\delta=.50$	$b_1(np\pi)$, $\delta=.58$	$b_2(np\pi)$, $\delta=.44$
2.719	2.174	2.304	2.074
1.283	1.088	1.145	1.035
.748	.657	.686	.625
.487	.435	.444	.424

Set II

$a_1(ns\sigma)$, $\delta=.86$	$a_1(np\sigma)$, $\delta=.45$	$b_2(np\pi)$, $\delta=.42$
2.973	2.086	2.044
1.360	1.058	1.029
.780	.641	.623
.495	.430	.423

Again, set II corresponds to the total charge shifted on to the doubly bonded carbons. The basis sets used in these calculations were as follows. First the hydrogen atoms were neglected, simplifying the calculations to that for a bent C_4 core.

For trans-butene a z axis was constructed passing through the midpoints of the two carbon-carbon single bonds, and the x axis was taken at right angles to this in the plane of the molecule. Gaussian functions were placed at centers located at the atomic centers and at the midpoint of the C_4 core. For the a_g(ns) and b_u orbital calculations these functions were:

Center	Exponent	Type
End Carbons	.45	s and p_z
	.15	
Midpoint	.45	s and p_z
	.15	
	.05	
	.0166	
	.0055	
	.0018	
	.0006	

For the other b_u orbital, these functions were:

Center	Exponent	Type
End Carbons	.0166	p_x
	.0055	
	.0018	
	.0006	
Center Carbons	.45	p_x
	.15	
	.05	

For the $a_u(np\pi)$ orbital calculations these functions were:

Center	Exponent	Type
End Carbons	.45	p_y
	.15	
	.05	
	.0166	
	.0055	
	.0018	
Center Carbons	.45	p_y
	.15	
	.05	

Finally for the $a_g(nd\sigma)$ orbital the functions were:

Center	Exponent	Type
End Carbons	.0166	p_z
	.0055	
	.0018	
	.0006	

Center	Exponent	Type
Center Carbons	.45	p_z
	.15	
	.05	

For the cis-butene calculations Gaussian functions were placed at each of the atomic centers, and at the center of gravity of the molecule. For the $a_1(ns)$, $a_1(np\sigma)$ and $b_2(np\pi)$ orbital calculations these functions were:

Center	Exponent	Type
Carbons	.45	s
Center of Gravity	.45	
	.15	s, p_x and p_z
	.05	
	.0166	
	.0055	
	.0018	
	.0006	

For the $b_1(np\pi)$ orbital calculations, these functions were

Center	Exponent	Type
Carbons	.45	p_y
	.15	
Center of Gravity	.05	p_y
	.0166	
	.0055	
	.0018	
	.0006	

When we compare the results of our calculations with the experimental series of McDiarmid, the interpretations are obvious. We interpret the two series containing the mystery bands to be ns series. These series are thus $^1A_u(ns\sigma)$ and $^1B_1(ns\sigma)$ series of trans and cis-butene respectively. In both cases the agreement between the calculations and experimental values is much improved when we use the set II calculations for comparison. This demonstrates that the trans and cis-butene spectra are really perturbed ethylene spectra. In the future, we intend to make more use of this principle in isolating the important regions in a molecule from the general molecular framework. We note that our interpretation of these series concurs with that given by McDiarmid.

Her interpretation of the other Rydberg series in trans-butene is that is an nd series. Our calculations fix it specifically as an ndσ series, where the sigma axis is along the z axis which we have described for trans-butene above. We then assign this series as $^1A_u(nd\sigma)$.

REFERENCES

1. R. McDiarmid, J. Chem. Phys., 50, 2328 (1968).

4.21 BENZENE

The ground state of benzene $\tilde{X}$ is a planar regular hexagon (symmetry D_{6h}), and the same is true of its Rydberg states. Thus the selection rules for dipole allowed transitions from the ground state are:

$$A_{2u} \leftarrow \tilde{X} \qquad \text{z transition}$$
$$E_{1u} \leftarrow \tilde{X} \qquad \text{x, y transition}$$

Infrared and raman spectroscopy yield the following geometrical parameters for the ground state $\tilde{X}$:

$$C\text{–}C \sim 2.640 \text{ a.u.}$$
$$C\text{–}H \sim 2.048 \text{ a.u.}$$

The orbital energies for benzene have been calculated by several authors. They can be summarized by a Table taken from Buenker, Whitten and Petke.[1]

	Buenker et al.	Schulman and Moskowitz	Schulman and Moskowitz
$1a_{1g}$	-11.354	-10.78	-11.30
$1e_{1u}$	-11.354	-10.77	-11.30
$1e_{2g}$	-11.353	-10.77	-11.29
$1b_{1u}$	-11.352	-10.77	-11.29
$2a_{1g}$	- 1.173	- 0.990	- 1.168

	Buenker et al.	Schulman and Moskowitz	Schulman and Moskowitz
$2e_{1u}$	- 1.043	- 0.891	- 1.037
$2e_{2g}$	- 0.848	- 0.714	- 0.846
$3a_{1g}$	- 0.741	- 0.571	- 0.738
$2b_{1u}$	- 0.674	- 0.563	- 0.662
$1b_{2u}$	- 0.660	- 0.448	- 0.654
$3e_{1u}$	- 0.626	- 0.479	- 0.622
$1a_{2u}(\pi)$	- 0.538	- 0.452	- 0.535
$3e_{2g}$	- 0.526	- 0.374	- 0.524
$1e_{1g}(e)$	- 0.379	- 0.288	- 0.373
E_T	-230.3745	-220.068	-230.463

Thus the electronic configuration of the ground state $\tilde{X}$ is:

$$\{\text{core}\}\ (1e_{1g})^4 - {}^1A_{1g}$$

where $\{\text{core}\}$ consists of the orbitals:

$$(1a_{1g})^2(1e_{1u})^4(1e_{2g})^4(1b_{1u})^2(2a_{1g})^2(2e_{1u})^4(2e_{2g})^4$$
$$\text{x}\ (3a_{1g})^2(2b_{1u})^2(1b_{2u})^2(3e_{1u})^4(1a_{2u})^2(3e_{2g})^4$$

and the electronic configuration of the Rydberg states converging to the first ionization limit of benzene is:

$$\{\text{core}\}\ (1e_{1g})^3(nR)$$

Thus the dipole allowed transitions are $A_{2u}(e_{1u})$ and $E_{1u}(a_{2u})$; where the symmetries in parenthesis are the symmetries of the Rydberg orbitals.

The optical spectrum of benzene begins at 2600 Å with a much studied band system due to the transition $\tilde{A} \leftarrow \tilde{X}$. This system was the first extensive and clear cut example of an electronic transition forbidden by symmetry selection rules and was only explained after consideration of vibronic interaction as a $^1B_{2u}[\{core\}(1e_{1g})(1e_{2u})] \leftarrow \tilde{X}$ transition.

In the region 2050 Å to 1800 Å there are at least two electronic transitions. One, designated as $\tilde{B} \leftarrow \tilde{X}$ is described as either an $^1E_{2g}[\{core\}(1e_{1g})^3(1b_{2g})]$ or $^1B_{1u}[\{core\}(1e_{1g})^3(1e_{2u})] \leftarrow \tilde{X}$ transition. The other, $\tilde{C}$, at shorter wavelengths is an $^1E_{1u}[\{core\}(1e_{1g})(1e_{2u})] \leftarrow \tilde{X}$ transition.

Lying on top of $\tilde{C}$ is $\tilde{D}$ the first member of one of four Rydberg series converging to the first ionization limit. Wilkinson[2] gives these series as:

nR			nR′		
$74587 - R/(n - .46)^2$			$74587 - R/(n - .16)^2$		
n		I.P. − ν	n		I.P. − ν
(3)	$\tilde{D}$	2.32	(3)	$\tilde{E}$	1.84
(4)	$\tilde{H}$	1.10	(4)	$\tilde{I}$	.88
(5)		.66	(5)		.56
(6)		.44	(6)		.39
I.P. = 9.245 eV			I.P. = 9.245 eV		

nR″		nR‴	
$74587 - R/(n - .11)^2$		$74587 - R/(n - .04)^2$	
n	I.P. = ν	n	I.P. - ν
(3) $\tilde{F}$	1.63	(3) $\tilde{G}$	1.26
(4) $\tilde{J}$	.87	(4) $\tilde{K}$	.86
(5)	.56	(5)	.55
I.P. = 9.245 eV		I.P. = 9.245 eV	

The nR and nR′ series are strong, while the nR″ and nR‴ series are weak in intensity. Furthermore, many of the members of these series show vibrational substructure under high resolution.

In addition to these series converging to the first ionization limit, two Rydberg series have been reported[3] as converging to a limit at 11.489 eV, and another to a different limit at 16.84 eV. However, as no further details of these series were given, we cannot assign them on the basis of the optical spectrum.

The results of model calculations on benzene are as follows:

nsa_{1g}, $\delta = .68$	npa_{2u}, $\delta = .49$	npe_{1u}, $\delta = .35$
2.52	2.16	2.03
1.21	1.09	1.02
.71	.66	.62
.47	.44	.42

nda_{1g}, $\delta = .40$	nde_{1g}, $\delta = .04$	nde_{2g}, $\delta = .02$
2.01	1.40	1.38
1.01	.87	.86
	.60	.58

The basis sets used were as follows. The hydrogens were neglected, reducing the calculation to that for a C_6 core. Gaussian functions were placed at various centers both at and exterior to the atomic centers. For the nsa_{1g} orbitals these centers and functions were:

Center	Exponent	Type
(-5.272, 0.0, 0.0)[a] [C_6][b]	.45	s
	.15	
(0.0, 0.0, 0.0) [E]	.05	s
	.0166	
	.0055	
	.0018	
	.0006	
	.0002	

For the npa_{2u} orbitals they were:

Center	Exponent	Type
(-6.0, 0.0, 0.0) [C_6]	.45	p_z
	.15	

(a) (x, y, z) coordinates locating the basis function.

(b) Symmetry operation in D_{6h} locating points with identical basis functions.

Center	Exponent	Type
(0.0, 0.0, 0.0) [E]	.05	p_z
	.0166	
	.0055	
	.0018	
	.0006	
	.0002	

For the npe_{1u} orbitals they were:

Center	Exponent	Type
(-4.0, 0.0, 0.0) [C_2]	.45	p_y
	.15	
(0.0, 0.0, 0.0) [E]	.05	p_y
	.0166	
	.0055	
	.0018	
	.0006	
	.0002	

For the nda_{1g} orbitals they were:

Center	Exponent	Type
(0.0, 0.0, 1.0) [σ_h]	.45	p_z
	.15	
	.05	
(0.0, 0.0, 4.0) [σ_h]	.0166	p_z
	.0055	
	.0018	
	.0006	

For the nde_{1g} orbitals they were:

Center	Exponent	Type
(-2.636, 0.0, 0.0) [C_2]	.15	p_z
	.05	
	.0166	
(-6.0, 0.0, 0.0) [C_2]	.0055	p_z
	.0018	
	.0006	
	.0002	

Finally, for the nde_{2g} orbitals they were:

Center	Exponent	Type
(-2.636, 0.0, 0.0) [C_2]	.15	p_y
	.05	
	.0166	
(-6.0, 0.0, 0.0) [C_2]	.0055	p_y
	.0018	
	.0006	
	.0002	

The interpretation of the optical spectrum of benzene goes as follows. The strong nR and nR′ series would seem to be due to the dipole allowed a_{2u} and e_{1u} series. The best fit is with the nR series assigned as npa_{2u} and the nR′ series as npe_{1u}. This would make the nR series due to $^1E_{1u}(a_{2u})$ and the nR′ series due to $^1A_{2u}$ (e_{1u}) states.

The other two weak nR″ and nR‴ series must be due to dipole forbidden transitions. The possibilities are the nsa_{1g}, the nda_{1g}, the nde_{1g} and the nde_{2g} series. Looking at our calculations, we see that the latter two series agree best with the nR″ and nR‴ series, although the agreement is not perfect. We then assign the nR″ series as nde_{1g} and the nR‴ series as nde_{2g}, making the states $^1A_{1g}(e_{1g})$ and $^1B_{1g}(e_{2g})$ respectively. These assignments could, however, be reversed, and still agree reasonably with our calculations.

This concludes the work that can be done with the optical spectrum. The electron impact spectrum has been taken for benzene by Lassettre et al.[4] and shows new features which need to be interpreted. Lassettre's spectrum is reproduced in Figure 1, together with our proposed assignment of the peaks.

It is clear from the spectrum that the portion below 9.2 eV is similar to the dipole allowed optical spectrum. In general, this will be true for an electron impact spectrum at high incident electron energy and small scattering angle. Thus to interpret the rest of the spectrum we need to know the symmetries of the dipole allowed Rydberg orbitals corresponding to excitation from the different orbitals of the benzene core. This has been done nicely by Jonsson and Lindholm,[5] and we reproduce part of their table below:

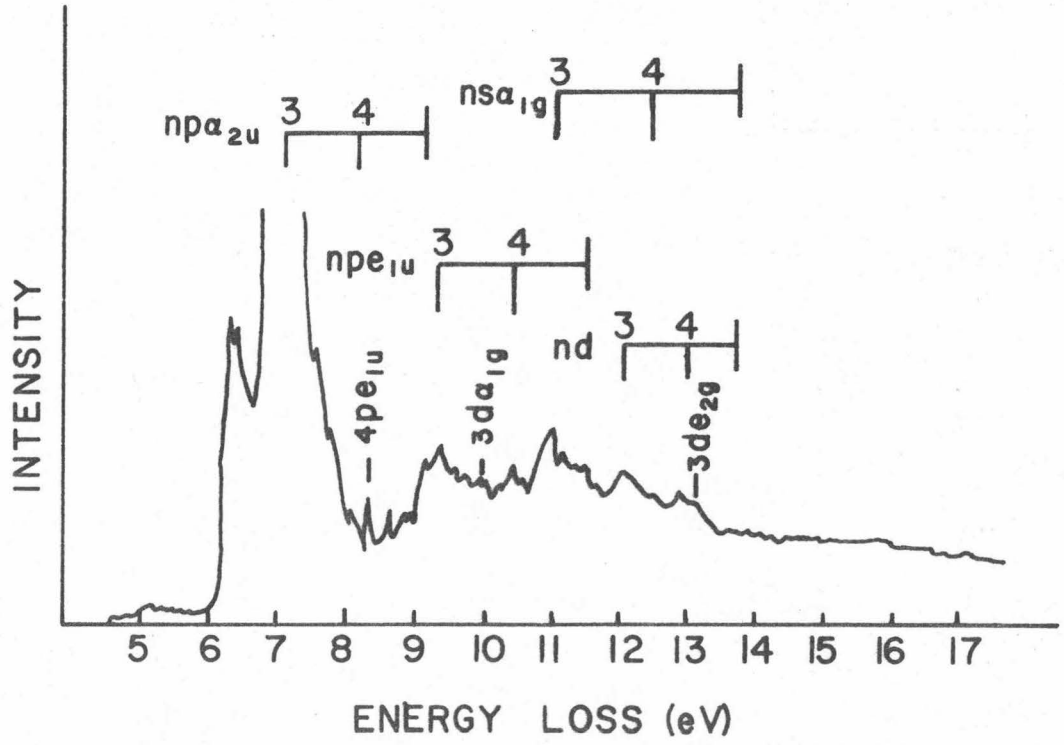


Figure 1. Electron Impact Spectrum of Benzene

Initial Orbital of Electron	Proposed Orbital Energy	Dipole Allowed Rydberg Orbital
$1e_{1g}$	9.3[a] eV	npe_{1u}
		npa_{2u}
$3e_{2g}$	11.4	npe_{1u}
$1a_{2u}$	12.1	nsa_{1g}
		nda_{1g}
		nde_{1g}
$3e_{1u}$	13.8	nsa_{1g}
		nda_{1g}
		nde_{1g}
		nde_{2g}
$1b_{2u}$		nde_{2g}

(a) As measured by photoelectron spectroscopy.

Using this table together with our calculations we assign the peaks at 7.0 and 8.2 eV as $1e_{1g} \rightarrow 3pa_{2u}$ and $4pa_{2u}$ transitions, respectively, and those at 7.4 and 8.4 eV as $1e_{1g} \rightarrow 3pe_{1u}$ and $4pe_{1u}$. Our results confirm the assignment of the peak at 11.4 eV in the photoelectron spectrum, also observed optically, as the $3e_{2g}$ level since this leads to transitions $3e_{2g} \rightarrow 3pe_{1u}$ and $4pe_{1u}$ at 9.4 and 10.4 eV, respectively, in good agreement with the experimental peaks, at 9.3 and 10.4 eV. We predict a $1a_{2u} \rightarrow 3da_{1g}$ transition at 10.1 eV,

correlating very well with the experimental peak at 10.0 eV. We would also assign the $3e_{1u} \rightarrow 3sa_{1g}$ and $3e_{1u} \rightarrow 3d_{1g}$ or $3de_{2g}$ transitions, calculated at 11.3 and 12.4 eV, to the strong peaks at 11.0 and 12.2 eV respectively in the energy loss spectrum. The small unassigned peak at 12.6 eV is very probably the $3e_{1u} \rightarrow 4sa_{1g}$ transition predicted at 12.6 eV. Finally, the peak at 12.9 eV could also be the $3e_{1u} \rightarrow 4d$ transition. The calculated term values put the $3e_{1u} \rightarrow 4d$ transition at 12.9 eV and the proposed $1b_{2u} \rightarrow 3de_{2g}$ assignment at 13.1 eV.

It remains to compare our benzene assignments with those of Jonsson and Lindholm. In general, our results agree with theirs. We both agree with one another and with the orbital energy calculations as to the ordering of the various orbitals in benzene. Our sharpest difference occurs in the interpretation of the dipole allowed transitions converging to the first ionization limit. Our assignment of the peaks is just contrary to Jonsson Lindholm's which is the usual assignment given. However, Liehr and Moffitt, [6] agree with our interpretation, and show how this assignment can lead to the experimental vibrational substructure which is observed in these bands.

The other difference is minor. We suggest that the transition assigned as $1b_{2u} \rightarrow 3de_{2g}$ by Jonsson and Lindholm could be a $3e_{1u} \rightarrow 4d$ transition while the $1b_{2u} \rightarrow 3de_{2g}$ would lie close by at slightly higher energy. Other than this our assignments agree completely.

REFERENCES

1. R. J. Buenker, J. L. Whitten, J. D. Petke, J. Chem. Phys., 49, 2261 (1968).
2. P. G. Wilkinson, Can. J. Phys., 34, 596 (1956).
3. M. A. El-Sayed, M. Kasha, Y. Tanaka, J. Chem. Phys., 34, 334 (1961).
4. E. N. Lassettre, A. Skerbele, M. A. Dillon and K. J. Ross, J. Chem. Phys., 48, 5066 (1968).
5. B. Ö. Jonsson, E. Lindholm, Arkiv för Fysik, 39, 65 (1967).
6. A. D. Leihr, W. Moffitt, J. Chem. Phys., 25, 1074 (1956).

5. Conclusions

In the preceding sections pertaining to individual molecules we have stated our interpretations of our results for each molecule separately. In this section we would like to consider these results as a whole and present the highlights of some of the more important results.

This space is too short to include more than a brief mention of all of the states to which we have assigned symmetries. In carbon dioxide, for instance, we have been able to assign symmetries to all of the observed Rydberg series. This is more impressive when we remember that previous to this, none of the symmetries of any of these series had been assigned. This, despite the fact that carbon dioxide has been the subject of spectroscopic investigations for many years. Again, in the case of 1, 3-butadiene we were able to fit previously isolated bands into several different Rydberg series, give them symmetry designations, and lend support to a previously doubted cis-butadiene Rydberg series as a consequence of our calculations. These are not atypical results. For practically every molecule that we considered we were able to supply new symmetry assignments for the observed Rydberg series, and to suggest assignments for previously isolated bands.

In the following we would like to consider some specific aspects of our work on the carbon monoxide, nitric oxide, ethylene and benzene molecules. We concentrate especially on the

areas where our calculations were able to offer confirmation or to suggest new interpretations for experimental work. In several ways, our method is at its best when used in this fashion as an adjunct to experimental methods.

We consider carbon monoxide first. Converging to the first ionization limit of carbon monoxide at 14.001 eV are the states:[1]

State	Term value
B ($^1\Sigma^+$)	10.777
b ($^3\Sigma^+$)	10.393
F ($^1\Sigma^+$)	12.364
C ($^1\Sigma^+$)	11.397
c ($^3\Sigma^+$)	11.415
E ($^1\Pi$)	11.521

On the basis of our calculations, we were able to recognize the states B and F as the first two members of an nsσ Rydberg series. This was important because previously the state F had been classified as a $^1\Pi$ state. This fact in turn threw doubt upon the classification of the E state previously classified as a $^1\Sigma^+$ state since only two $^1\Sigma^+$ states are expected in this region. Our conclusions as to these assignments have been confirmed both experimentally by Tilford, Vanderslice and Wilkinson,[2] and by the calculations of LeFebvre Brion, Moser and Nesbet.[3] The F

state has been definitely confirmed as a $^1\Sigma^+$ state and the E state has been re-assigned as a $^1\Pi$ state.

In the case of the nitrogen dioxide molecule, another interesting situation connected with Rydberg states converging to the first ionization potential arose. The ground state of nitrogen dioxide is bent, the ∠ ONO angle is approximately 134°. However, the nitrogen dioxide ions are isoelectronic with carbon dioxide and are therefore linear. This large change in geometry in going from ground to excited states makes identification of Rydberg series for this molecule extremely difficult. In fact, the nitrogen dioxide spectrum in the region below the first ionization potential (1650-1350 Å) consists of an extensive system of fairly sharp bands which bears little resemblance to the usual Rydberg spectrum.

Ritchie and Walsh[4] made a careful study of these bands and concluded that they represented a lower member of a linear Rydberg state with symmetry $^2\Sigma_u^+$. Using this fact, together with our calculated value of 2.5 eV for the 3pσ Rydberg orbital, we were able to suggest a value for the ionization potential of 9.73 eV for nitrogen dioxide. This substantiates the observation of Nakayama, Kitamura and Watanabe[5] who observed a weak photoionization at 9.78 eV and attributed it to the first ionization limit. At the same time it eliminates the possibility of this limit at 10.83 eV which had been suggested earlier and is attributed to the dissociation $NO_2 + h\nu \rightarrow NO^+ + O^-$ by the above authors.

The results which we obtained for ethylene can be applied to several problems of current interest in connection with that molecule. One such problem is the characterization of the V state. Rydberg states can be quite close to or even on top of valence-shell transitions. Experimentally such situations can usually be identified, but ambiguities can arise in correlating Hartree-Fock excited state spectra with the observed transitions. For ethylene, our calculations show a Rydberg state 1.52 eV below the energy of the $C_2H_4^+$ ion or 9.0 eV above the ground state. This state is of the same symmetry as the V state of the $\pi^* \leftarrow \pi$ transition observed at 7.6 eV above the ground state. We ask, where do these states lie in the Hartree-Fock approximation? The Rydberg (π, π^*) state must be at approximately 1.52 eV below the HF energy of $C_2H_4^+$. But direct SCF calculations give a Hartree-Fock ionization potential of 9.05 eV putting this Rydberg state of the same symmetry as the V state at 7.53 eV above the ground state in the Hartree-Fock approximation.[6] In fact, in the Hartree-Fock approximation the lowest state of (π, π^*) symmetry is a Rydberg state whereas spectroscopically the lowest state of this symmetry is the strong valence shell transition at 7.6 eV with oscillator strength of 0.34.

Another problem associated with ethylene, or more properly with substituted ethylenes, is that of the so-called mystery band. This band is apparent in trans and cis-butene, for instance, at about 49000 cm^{-1} slightly to the red side of the diffuse V $\leftarrow$ N $(\pi^* \leftarrow \pi)$ transition. Our calculations support the experimental

interpretation of McDairmid[7] that these bands correspond to 3s Rydberg states located about 3.0 eV below the ionization limit.

As a final illustration of our results we want to mention the Rydberg series converging to the first ionization limit of benzene. There are two strong Rydberg series converging to this limit which must correspond to the dipole allowed E_{1u} and A_{2u} series. The problem is to decide which is which. Since the lowest state of one of these series, $\tilde{C}$, lies directly on top of another state, $\tilde{D}$, of known E_{1u} symmetry, it has been assumed that the series containing this member must be of symmetry A_{2u}.[8]

Our calculations, however, indicated very strongly that this assignment was incorrect, and the state $\tilde{C}$ should be of the same symmetry as the state $\tilde{D}$. We then argued that the two states were so dissimilar that there was very little interaction between them, and hence one could be seen lying on top of the other. We were very pleased, then, when Schnepp, et al.,[9] suggested confirmation of our results with their circular dichroism measurements on benzene.

The above results illustrate how our calculations have and can in the future contribute to our knowledge of chemical systems. We feel that the speed, flexibility and accuracy of our method will make it useful for many chemists, both theorists and experimentalists.

References

1. Y. Tanaka, A. S. Jursa, and F. LeBlanc, J. Chem. Phys. 26, 862 (1957).
2. S. G. Tilford, J. T. Vanderslice, P. G. Wilkinson, Can. J. Phys. 43, 450 (1965).
3. H. LeFebvre Brion, C. M. Moser, R. K. Nesbet, J. Mol. Spectrosc. 13, 418 (1964).
4. R. W. Ritchie, A. D. Walsh, Proc. Roy. Soc. 267A, 395 (1962).
5. T. Nakayama, M. Y. Kitamura, K. Watanabe, J. Chem. Phys. 30, 1180 (1959).
6. H. Basch and V. McKoy, J. Chem. Phys. 53, 1628 (1970).
7. R. McDairmid, J. Chem. Phys. 50, 2328 (1968).
8. B. Jonsson and E. Lindholm, Ark. Fysik 39, 65 (1969).
9. O. Schnepp, et al., private communication.

Appendix A

Rydberg States of Diatomic and Polyatomic Molecules Using Model Potentials

TIMOTHY BETTS AND VINCENT McKOY*

Arthur Amos Noyes Laboratory of Chemical Physics†

California Institute of Technology, Pasadena, California 91109

(Received 14 August 1970)

We have used a simple model potential to calculate Rydberg series in N_2, O_2, CO, NO, ethylene, and benzene. The model potential for a molecule is taken as the sum of atomic potentials, which are calibrated to atomic data and contain no further parameters. Our results agree with experimentally measured values to within 5-10% in all cases. We apply our results to several unresolved problems connected with the above molecules, and indicate some of the applications which we foresee for model calculations.

---

*Alfred P. Sloan Foundation Fellow.

†Contribution No. 4118 .

I. INTRODUCTION

Recently the pseudopotential method has become increasingly popular as a method for obtaining approximate descriptions of atomic and molecular Rydberg states.[1] In particular, Hazi and Rice[2] have given a successful treatment of some Rydberg states of the hydrogen, nitrogen, and benzene molecules using a simple and physically appealing model potential. Conceptually we can think of using a pseudopotential formalism to satisfy any orthogonality conditions between the Rydberg orbital and the core functions. To do this one replaces the orthogonality constraints in the eigenvalue equation by adding a nonlocal pseudopotential to the single-particle Hamiltonian without changing the Rydberg orbital eigenvalue.[1] The formal pseudopotential equations can be just as difficult to solve exactly as the original equations. But, as stressed by Hazi and Rice,[2] it is possible to use simple model potentials to reproduce many advantages of the exact pseudopotential formalism. These model potentials simplify the computations considerably and, in fact, since they are calibrated to experimental data, include effects not considered in the formal theory.[1]

In this paper we use model potentials to study the Rydberg states of the diatomic molecules O_2, N_2, CO, NO and the polyatomic molecules ethylene and benzene. We assume that the effective potential of the molecular core can be represented by a sum of model potentials of the consituent atoms. However the parameters of the model potential

for each atom are determined by fitting its Rydberg spectrum to its experimental term values. The model potential for the molecule, expressed as a sum of these atomic potentials, contains no adjustable parameters. We then expand the Rydberg molecular orbital in terms of Gaussian-type orbitals located on each atomic center. The use of these basis functions provide both speed and flexibility for practical calculations on large polyatomic molecules. Most of the calculations reported in this paper can be done in a few minutes on a computer. The results are quite accurate, usually within five or ten percent of available experimental results. It is not our intention to develop a scheme of high accuracy but simply to illustrate that the use of model potentials can provide results of comparable accuracy to those of more tedious and elaborate approaches. It is obvious that a direct SCF calculation of Rydberg states of large polyatomic molecules is presently not feasible and would probably not be worthwhile in any event.

These results on molecular Rydberg states are useful in studying the valence excited states of the same symmetry in many polyatomic molecules. Rydberg states can be quite close to and even on top of valence-shell transitions. Experimentally such situations can usually be identified but ambiguities can arise in correlating the Hartree-Fock excited state spectra with the observed transitions. For example, our calculations show a Rydberg state in ethylene at 1.52 eV below the energy of $C_2H_4^+$ and therefore at 9.0 eV above the ground state.[3] This state is of the same symmetry as the V state of the N $\rightarrow$ V transition ($\pi \rightarrow \pi^*$)

observed at 7.6 eV above the ground state. We now ask where do these states lie in the Hartree-Fock approximation? The Rydberg (π, π^*) state must be at approximately 1.52 eV below the HF energy of $C_2H_4^+$. But direct SCF calculations give a Hartree-Fock ionization potential of 9.05 eV putting this Rydberg state of the same symmetry as the V state at 7.53 eV above the ground state in the Hartree-Fock approximation.[4] In fact, in the Hartree-Fock approximation the lowest state of (π, π^*) symmetry is a Rydberg state whereas spectroscopically the lowest state of this symmetry is the strong valence-shell transition at 7.6 eV with an oscillator strength of 0.34.

In the next section we begin with a discussion of the use of model and pseudopotentials in studying molecular Rydberg states. In section II we describe in detail the procedure for obtaining the parameters for the atomic model potential from spectroscopic tables. Section III is devoted to the related Rydberg spectra of the diatomics N_2, NO, O_2, and CO and section IV discusses the Rydberg spectrum of ethylene and its relation to valence excited states. Finally in section V we calculate the various Rydberg states of benzene and use these results to interpret the electron impact spectrum of that molecule.

II. THEORY

In a Rydberg transition an electron is excited to an orbital large in size relative to a singly charged core. Moreover the energy levels of these states can be expressed as

$$E_n = IP - R/(n - \delta)^2 \tag{1}$$

where IP is the ionization potential, R the Rydberg constant, and δ is the quantum defect which may vary slightly with n. From Eq. (1) we know that Rydberg states are essentially hydrogenic in character which implies that the molecular core produces the potential of a monopole. The quantum defect δ measures the departure from this simple hydrogenic model and correlates with how the nodes and loops of the Rydberg orbital are displaced relative to analogous hydrogenic nodes and loops. With these properties it is obvious how one should apply a pseudopotential formalism to study Rydberg states. In an independent particle approximation the Rydberg orbital, ψ_R, must be orthogonal to the core solutions of the one-electron Hamiltonian, H, i.e.,

$$H\psi_R = \epsilon_R \psi_R \tag{2a}$$

$$H\psi_c = \epsilon_c \psi_c \tag{2b}$$

$$\langle \psi_R, \psi_c \rangle = 0 \, . \tag{2c}$$

In pseudopotential theory one can replace the orthogonality constraints Eq. (2c), on the eigenvalue equation, Eq. (2a), by adding a pseudopotential

V_S to H and solving the new eigenvalue equation[5]

$$(H + V_S)\phi_R = \epsilon_R \phi_R \tag{3}$$

where ϕ_R is not subject to orthogonality constraints but the eigenvalue, ϵ_R, is unchanged. The Phillips and Kleinman V_S is the nonlocal operator

$$V_S = \sum_{\text{core}} (\epsilon_R - \epsilon_c) |\phi_c\rangle \langle\phi_c| \tag{4}$$

Equation (3) with V_S of Eq. (4) is probably no simpler to solve at a practical level than is Eq. (2a) with its constraints Eq. (2c). However, as stressed in Ref. 2, we can construct much simpler model potentials which reproduce the main characteristics of the formal pseudopotential. Model potentials are flexible and usually contain some adjustable parameters. The resulting equations for the eigenvalues are much simpler than those of Eq. (3). To account for Eq. (1) the model potential must go as $-1/r$ at large r. The potential must have the symmetry of molecular framework and also account for penetration and exclusion effects.

For atomic Rydberg states one could use the model potential suggested by Abarenkov and Heine[6]

$$\begin{aligned} V_M &= A && r < r_0 \\ &= \frac{\delta Z}{r} && r \geq r_0 \end{aligned} \tag{5}$$

where δZ is the effective charge of the atom. This potential is constant inside a sphere of radius r_0 and Coulombic outside of the sphere. The model potential is an approximate representation of the effective potential $V + V_S$ where V is the single-particle potential in the Hamiltonian H of Eq. (2a). For a reasonable choice of r_0 we can use V_M of Eq. (5) to solve for the atomic term values as a function of the parameter A. Comparison of the predicted term values with the experimental spectrum gives a unique choice for A. The only absolute requirement on a pseudo or model potential is that it reproduces the eigenvalues of the real potential. Clearly V_M of Eq. (5) is not a correct representation of the true $V + V_S$ at all points in space. Outside the core it is probably a good representation of the effective potential but certainly it does not represent any meaningful potential inside the core. The true effective potential must have a complicated form inside the core which we really do not need to know. For practical purposes a simple model potential such as Eq. (5) imposes the proper boundary conditions and can therefore reproduce the eigenvalue spectrum. For further discussion including a justification for choosing V_M of Eq. (5) as an atomic model potential see Ref. 1.

For molecular applications we want a model potential with no additional adjustable parameters. To apply this model potential, Eq. (5), to molecular Rydberg states we assume that the molecular model potential is a simple superposition of the atomic potentials. All parameters of the atomic V_M are fixed by calibration to atomic term values for each atom

separately. Hence

$$V_{Mol} = \sum_{atoms} V_{atom} \tag{6}$$

we have found that including a term in Eq. (6) to represent the hydrogen atom contribution has only a small effect on the eigenvalue spectrum. We will discuss this when we consider the ethylene spectrum. The results of the molecular calculation are also insensitive to the exact value of the atomic parameters.

We use Gaussian basis functions on the atomic and other centers to provide speed and flexibility in the numerical solution of the one-electron molecular problem. Although one has to use many such functions due to their incorrect asymptotic form we feel that their other properties, especially the ease of computation with high n values and their general diffuseness outweigh other considerations. For the molecular calculations we used a computer program adapted from one provided by Dr. N. Winter. It utilizes only S, P_x, P_y, and P_z basis functions but by placing these functions at other than atomic centers we can calculate molecular Rydberg states of various symmetries.

III. ATOMIC CALIBRATION

The solution of the one-electron Schrödinger equation for an atomic Rydberg state with V_M of Eq. (5) i.e.,

$$(- \tfrac{1}{2} \nabla^2 + V_{atom}) \psi_a^n = \epsilon_a^n \psi_a^n \tag{7}$$

is easy. Writing

$$\psi_a^n = (R^{n\ell}(r) \mid r) Y_{\ell m} (\theta, \phi) \tag{8}$$

we have

$$\frac{d^2 R_{n\ell}}{dr^2} + [b - \frac{\ell(\ell + 1)}{r^2}] R_{n\ell} = 0 \quad r < r_0 \tag{9}$$

and

$$\frac{d^2 R_{n\ell}}{dr^2} + [a + \frac{2}{r} - \frac{\ell(\ell + 1)}{r^2}] R_{n\ell} = 0 \quad r \geq r_0 \tag{10}$$

where

$$b = 2(\epsilon_a^n - A) \tag{11a}$$

$$a = 2 \epsilon_a^n \tag{11b}$$

solutions of Eq. (9) which vanish at r = 0, are simple polynomials in $\sin \sqrt{b}\, r$, $\cos \sqrt{b}\, r$, and $\frac{1}{\sqrt{b}.r}$ for $b > 0$, similar polynomials in

sinh $\sqrt{|b|}\, r$, cosh $\sqrt{|b|}\, r$, and $\frac{1}{\sqrt{|b|}\, r}$ for $b < 0$, and $r^{\ell+1}$ for $\epsilon_a^n = A$.

We denote the solution of Eq. (9) for a given A by $\eta_A^\ell(\epsilon_a, r)$.

Solutions of Eq. (10) are just the Coulomb functions which decay exponentially at large r

$$\chi^\ell(r) = {}^0U^\ell(r) + \gamma(N, \ell)\, {}^1U^\ell(r) \tag{12}$$

with $N = 1/\sqrt{|a|}$ and

$$\gamma(N, \ell) = \frac{N^{2\ell+1}\, \Gamma(N-\ell)\tan(N-\ell-1)\pi}{\Gamma(N+\ell+1)} \tag{13}$$

The functions ${}^0U_\ell$ and ${}^1U_\ell$ are regular and irregular respectively at $r = 0$ and are tabulated for $\ell = 0, 1, 2$; $-1.2 \leq a \leq -0.07$, $2.0 \leq r \leq 15$ by Blume et al.[7] They[7] also tabulate the functions

$${}^0D^\ell = r\,\frac{d}{dr}\,{}^0U^\ell, \qquad {}^1D^\ell = r\,\frac{d}{dr}\,{}^1U^\ell \tag{14}$$

over the same range. We require the logarithmic derivatives $\frac{d}{dr}\ln \eta_A^\ell(\epsilon_A, r)$ and $\frac{d}{dr}\ln \chi^\ell(\epsilon_A, r)$ to be equal at the boundary $r = r_0$. The intersection of these plots determine the values of a for which a solution $R_{n\ell}$ exists. In calibrating the atomic model potential we choose a series of A's and compare the eigenvalue spectrum with the experimental term values. We choose the parameter A which gives the best fit with experiment. Ideally A should be a function of ℓ but we find that in practice we need to consider only $\ell = 0$ in Eqs. (9) and (10). Conse-

quently we calibrate only to the atomic ns series.

In determining the parameters for carbon, nitrogen, and oxygen, we may choose A to give agreement with either the atomic singlet or triplet levels for carbon, doublet or quartet for nitrogen, and triplet or quintet for oxygen. Table I gives the A's for both choices. In practical calculations the results are insensitive to which calibration we choose. We therefore did not attempt any averaging of the term values or parameters A.

IV. DIATOMIC MOLECULES

We now discuss the application of this model potential to the calculation of various Rydberg states of the diatomic molecules nitrogen, oxygen, nitric oxide and carbon monoxide. Table II gives the parameters, A, of the model potential for the carbon, nitrogen, and oxygen cores. Each atomic core also has an effective charge $\delta Z = \frac{1}{2}$ (Eq. (5)). The Rydberg energy levels are just the eigenvalues of the model Hamiltonian

$$(-\tfrac{1}{2}\nabla^2 + V_{mol})\,\psi_n = \epsilon_n \psi_n \qquad (15)$$

where V_{mol} is a sum of atomic model potentials and therefore, has the symmetry of the molecular framework. Recall that all adjustable parameters are fixed by calibration to atomic data and that V_{mol} has no additional adjustable parameters. Next we expand the Rydberg molecular orbital, ψ_n, as a linear combination of Gaussian-type orbitals. These

orbitals can be placed at arbitrary centers including the atomic centers and the midpoint of the bond. We will see that in other polyatomic systems the Gaussian orbitals can be placed at points completely off the molecular framework. We use only S and p-like orbitals with radial parts of the form $\exp(-\alpha r^2)$ and $r \exp(-\beta r^2)$ respectively. Table III lists the exponents α and β which we used for all calculations on diatomic molecules. The basis set includes some very diffuse functions which can adequately describe the high members of various Rydberg series. We have experienced no instability problem with these diffuse functions. More importantly, the use of Gaussian functions allows us to extend this method to large polyatomic molecules since the necessary integrals for such calculations are easily evaluated for a Gaussian basis set.

The ground state of N_2, $(X\,^1\Sigma^+g)$, has the electron configuration $(1\sigma_g)^2\,(1\sigma_u)^2\,(2\sigma_g)^2\,(2\sigma_u)^2\,(1\pi_u)^4(3\sigma_g)^2$. We consider Rydberg orbitals of the following symmetry $ns\sigma_g$, $np\sigma_u$, $np\pi_u$, $nd\sigma_g$, and $nd\pi_g$. The experimentally observed Rydberg states correspond to an electron in one of these orbitals and one of the following three cores

$$(1\sigma_g)^2\,(1\sigma_u)^2\,(2\sigma_g)^2\,(2\sigma_u)^2\,(1\pi_u)^4\,(3\sigma_g) \qquad X^2\,\Sigma_g^+$$

$$(1\sigma_g)^2\,(1\sigma_u)^2\,(2\sigma_g)^2\,(2\sigma_u)^2\,(1\pi_u)^3\,(3\sigma_g)^2 \qquad A^2\,\Pi_u$$

$$(1\sigma_g)^2\,(1\sigma_u)^2\,(2\sigma_g)^2\,(2\sigma_u)\,(1\pi_u)^4\,(3\sigma_g)^2 \qquad B^2\,\Sigma_u^+$$

In our simple model we assume these three cores to be identical and therefore specified by the same atomic model potentials. With the basis

functions of Table III we solve Eq. (15) for Rydberg eigenvalues using the Jacobi method for matrices. Table IV gives the results measured in electron volts below any of the three ionization potentials, 15.58, 16.69, and 18.76 eV for the $X^2\Sigma_g^+$, $A^2\Pi_u$, and $B^2\Sigma_u^+$ states of N_2^+ respectively.

The results are encouraging. We can readily identify four Rydberg series in good agreement with the available experimental data. These are the ns series with a term defect $\delta = 1.1$, npσ series with $\delta = 1.71$, npπ series with $\delta = 0.73$, and the ndσ series with $\delta = 1.75$. With the simple model potential and Gaussian functions we obtain four members of each series with a few minutes of computer time. The $3S\sigma_g$ is the only member of the ns series well identified experimentally. Our predicted term value of 3.80 eV agrees well with the experimental values of 3.4 and 3.71 eV for the $^1\Sigma_g^+$ and $^3\Sigma_g^+$ states arising from a $3\sigma_g \rightarrow ns\sigma_g$ transition, and the 3.59 and 3.89 eV for the $o\,^1\Pi_u$ and $^1\Sigma_u^+$ states arising from $1\pi_u \rightarrow ns\sigma_g$ and $2\sigma_u \rightarrow ns\sigma_g$ transitions respectively. For the npσ series the $4p\sigma_u$ to $7p\sigma_u$ members have been identified experimentally. The calculated term values for this series are in good agreement with these results. The calculated term value for the lowest member of the ndσ series is 2.70 eV. Mulliken has suggested that the $h\,^1\Sigma_u^+$ state at 13.98 eV above the ground state of N_2 may be a member of the ndσ series with configuration (core) $(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2(nd\sigma_g)$. This state then has a term value of 2.71 eV in very good agreement with our

predicted term value of 2.70 for the $4d\sigma_g$ Rydberg state. Finally, no member of the $nd\pi$ series has been definitely identified. The calculated term value for the first member of this series i.e., $4d\pi_g$ orbital, is 2.52 eV. This does rule out the possibility that the state observed at 13.184 eV with a $A^2\Pi_u$ core $[(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2]$ could be a $^1\Sigma_u^+$ state since the Rydberg orbital would necessarily be π_g $(4d\pi_g)$ and consequently should lie at about 14.2 eV.

Finally the calculated term values in Table IV agree very well with those obtained by Lefebvre-Brion and Moser[9] by direct Hartree-Fock calculations. For example, some term values obtained from their Table III–V are 3.68 and 1.68 eV for the $3s\sigma_g$ and $4s\sigma_g$ members of the ns series; 2.48, 1.18, and 0.68 eV for the $4p\sigma_u$, $5p\sigma_u$, and $6p\sigma_u$ members of the $np\sigma$ series, 2.48, 1.08, and 0.58 for the $3p\pi_u$, $4p\pi_u$, and $5p\pi_u$ members of the $np\pi$ series. The term values for the higher members of the Rydberg series can be obtained much more economically by our procedure than by direct Hartree-Fock calculations.

Next we consider the Rydberg spectrum of O_2. The ground state of O_2 $(^3\Sigma_g^-)$ has the electron configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2$. Again we calculate term values for states with Rydberg orbitals of the following symmetries $ns\sigma_g$, $np\sigma_u$, $np\pi_u$, $nd\sigma_g$, and $nd\pi_g$. The possible configurations and states of the ions to which these series converge are[10, 11]

$(\text{core})(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)$	$X^2\Pi_g$
$(\text{core})(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^3(1\pi_g)^2$	$a^4\Pi_u$ and $A^2\Pi_u$, etc.
$(\text{core})(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)(1\pi_u)^4(1\pi_g)^2$	$b^4\Sigma_g^-$ and $B^2\Sigma_g^-$, etc.
$(\text{core})\ (2\sigma_g)^2(2\sigma_u)(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2$	$c^4\Sigma_u^-$, etc.

The ionization potentials of these states are 12.08 eV($^2\Pi_g$), 16.11 eV and 16.82 eV($^4\Pi_u$, $^2\Pi_u$), 18.17 eV and 20.31 eV($^4\Sigma_g^-$, $^2\Sigma_g^-$), and 24.56 eV($^4\Sigma_u^-$). The simple model potentials we use do not distinguish between these various cores. In Table V we therefore, list the term values by the symmetry of the Rydberg orbital.

We can identify four Rydberg series in agreement with available experimental data and Leclercq's calculations.[12] These are the ns series with a term defect $\delta = 1.15$, npσ series with $\delta = 1.73$, npπ series with $\delta = 0.74$, and the ndπ series with $\delta = 1.04$. Unlike N_2 the nsσ_g series is well identified from n=3 to 6. Agreement with experiment is good for the series converging to the $^4\Pi_u$ or $^2\Pi_u$ state of O_2^+.[13] Codling and Madlen[11] report a ns series converging to the $c^4\Sigma_u^-$ state of O_2^+ but with term values of 1.70, 0.93, and 0.59 eV. They assign an observed state with a 3.70 eV term value to the ndπ series. Our results for the ns and ndπ series clearly show that the state with a term value of 3.70 eV belongs to the ns series. In Table V we have not listed the calculated term values for the npπ series since they are almost identical with the npσ series. The agreement with experiment is again good. The npσ and npπ have not been clearly distinguished experimentally since they both lead to dipole-allowed states, $^3\Sigma_u^-$, and $^3\Pi_u$.

Table IV lists the results of similar calculations for the Rydberg states of CO. The ground state configuration of CO($^1\Sigma^+$) is $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$. We calculate term values for states with

Rydberg orbitals of the following symmetries $ns\sigma$, $np\sigma$, $np\pi$, and $nd\pi$. The three possible cores for these Rydberg series are

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma) \qquad X^2\Sigma^+$$
$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^3(5\sigma)^2 \qquad A^2\Pi$$
$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)(1\pi)^4(5\sigma)^2 \qquad B^2\Sigma^+$$

which lie at 14.01, 16.54, and 19.67 eV above the ground state of CO. As before, the simple molecular model potentials we use do not distinguish between these various cores. We can readily identify three Rydberg series in agreement with experiment. These are the $ns\sigma$ series with $\delta = 1.08$, the $np\sigma$ series with $\delta = 1.73$ and the $np\pi$ series with $\delta = 0.74$. The state with $3s\sigma$ orbital is clearly the $B^1\Sigma^+$ state. Our calculated term value for the second member of the $ns\sigma$ series is 1.57 eV i.e., at 12.44 eV, confirming that the state at 12.264 eV, is not the $F^1\Pi$ state but a Σ state.[15,16] The $5p\sigma$, $6p\sigma$, and $7p\sigma$ members of the $np\sigma$ series and similarly the $np\pi$ series are in good agreement with the diffuse and sharp series respectively of Tanaka's β bands.[14] The Π state [($X^2\Sigma^+$ core) $3p\pi$] with a term value of 2.49 eV was previously identified as the $E^1\Sigma^+$ state. This confirms the reassignment suggested in reference 15. In studying the Rydberg series converging to the $B^2\Sigma^+$ state of CO^+ Ogawa observed two new series in addition to the Tanaka's sharp and diffuse series of the β band. These series (III and IV) have not been assigned In both cases the observed Rydberg bands are due to transitions between

anupper $^1\Sigma^+$ or $^1\Pi$ state and the $X^1\Sigma^+$ ground state of CO. Configurations [$(B^2\Sigma^+$ core) $np\pi$] and [$(B^2\Sigma^+$ core)$np\sigma$] have already been assigned to the upper state of Tanaka's sharp and diffuse series. We suggest that the electron configuration of the upper state in series IV is [$(B^2\Sigma^+$ ion) $nd\pi$], $^1\Pi$. The calculated $5d\pi$ and $6d\pi$ term values agree well with such an assignment but there is a 0.15 eV difference between the calculated and the proposed experimental term value for the $4d\pi$ member. This is probably within the limits of accuracy of our model. For the Rydberg series III[14] with term values 1.47, 0.83, 0.53, and 0.37 eV we propose an electron configuration [$(B^2\Sigma^+$ core) $ns\sigma$], n = 4, 5, 6, and 7. This is in fair agreement with the calculated term values of 1.57, 0.86, and 0.52 eV for the $4s\sigma$, $5s\sigma$, and $6s\sigma$ numbers.[17]

Finally we have calculated term values for possible Rydberg series of the NO molecule. The experimentally observed Rydberg states converge to one of the following ions.

$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(1\pi)^4$	$^1\Sigma^+$
$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(1\pi)^3 2\pi$	$a^3\Sigma^+$
$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)(1\pi)^4 2\pi$	$^1\Pi$

lying at 9.27, 14.22, and 18.33 eV above the ground state of NO. There is another state of unknown symmetry with the same configuration as the $a^3\Sigma^+$ at 16.56 eV. This is the limit of Tanaka's β series. From Table VII the calculated term values of the $ns\sigma$ and $np\sigma$ series with term defects 1.13 and 1.72 respectively agree very well with experiment. The $C^2\Pi$ and $K^2\Pi$ states are clearly the first and second members of the $np\pi$ series. The $D^2\Sigma^+$ and $M^2\Sigma$ are listed as having the united atom

forms [($^2\Sigma^+$ core) 4dσ and 5dσ] although at the equilibrium distance the separated atom forms σ3p and σ4p may be more appropriate.[19] The calculated term values are in good agreement with those calculated by direct matrix Hartree-Fock techniques for the Rydberg series converging to the $^1\Sigma^+$ ion.[20]

V. POLYATOMIC MOLECULES

A. Ethylene

The use of these simple model potentials and Gaussian orbitals makes it possible to study the Rydberg series of polyatomic molecules quite easily. First we consider the possible Rydberg states of ethylene. This example illustrates the need for being able to systematically sort out Rydberg states from valence-shell excited states in an SCF calculation of these states. Wilkinson has studied the Rydberg spectra in some detail.[21]

In its ground state the ethylene molecule is planar. With the x-axis perpendicular to the plane of the molecule and the z-axis along the C—C bond the electronic configuration of the ground state in D_{2h} symmetry is

$$(\Sigma)\,(1b_{3u})^2 = (1a_g)^2\,(1b_{1u})^2\,(2a_g)^2\,(2b_{1u})^2\,(1b_{2u})^2\,(3a_g)^2\,(1b_{3g})^2\,(1b_{3u})^2 \tag{16}$$

The $1b_{3u}$ orbital is the π MO. Excitation of an electron from the π MO to the π^* MO gives a $^3B_{1u}$ and $^1B_{1u}$ state. These are the spectroscopic T and V states respectively. The π^* MO is the $1b_{2g}$ orbital. We consider Rydberg states converging to the $C_2H_4^+$ ion with configuration $(\Sigma)\,(1b_{3u})$, $^2B_{3u}$, which lies at 10.52 eV above the ground state. For dipole-allowed transitions the Rydberg (upper) state must be B_{3u}, B_{2u}, or B_{1u} with x, y, and z polarization respectively. In B_{3u} states the Rydberg orbital is an a_g orbital. The a_g orbital becomes an ns orbital

in the united atom limit. Similarly for B_{2u} states the Rydberg orbital is of symmetry b_{1g} and this becomes nd_{xy} ($nd\delta$) in the UAO limit. The B_{1u} state has a Rydberg orbital of b_{2g} symmetry which becomes nd_{xz} ($nd\pi$) in the united atom limit. Note that the spectroscopic V state also has $^1B_{1u}$ symmetry. We will also calculate term values for the dipole forbidden states of configuration $(\Sigma)\ (1\pi)(np_x,\ np_y,\ \text{or}\ np_z)$.

The model potential for the molecular core is to be the sum of atomic model potentials with no additional adjustable parameters. The model potential of the positive ion core of ethylene would then be approximated by the sum of the model potentials of the two carbon atoms and the four hydrogen atoms in their appropriate valence states. On a physical basis we can expect the term values of Rydberg series for ethylene to depend only very slightly on the contribution of the hydrogen atoms to the molecular model potential. To show this and to assess the dependence of term values on the parameters of the carbon atom model potential we calculated the ns term values for three different model situations. The results are shown in Table VIII. Those in the first column are those obtained using the singlet parameters for the carbon core while those in the second column are obtained using the triplet parameters for the carbon core.[22] In both cases hydrogen atom contributions were neglected. The results in the third column are those of a model which attempts in a very crude fashion to include the effect of the hydrogen atom model potential by using a potential of the same form as Eq. (5) but with $A = 0.0$ and $\delta Z = 0.04$. This value of δZ is

consistent with Pauling's ideas on the ionic character of the C—H bond. The carbon singlet parameters were used but with $\delta Z = 0.42$. The basis set used in all calculations on ethylene is shown in Table IX. Clearly the term values depend only slightly on any potential due to the H-atoms and on small changes in the parameters of the C-atom potential. Hence for all calculations we used the C-atom singlet parameters and did not include any contribution to the core potential from the H-atoms.

Table X shows the term values for the various Rydberg series of ethylene. The calculated term values for the ns series agree well with Wilkinson's measurements.[21] Typical of ns series it shows a term defect of 1. This is his nR series.[21] Wilkinson identified three other Rydberg series all involving dipole-allowed upper states. These are the nR′, nR″, and nR‴ series. For a dipole-allowed transition the Rydberg orbital must be a_g, b_{1g}, or b_{2g}. The calculated term values for the ndσ series i.e., 2.32 and 1.15 eV, agree very well with those of the nR′ series, 2.26 and 1.16 eV. We therefore assign Wilkinson's nR′ series as a ndσ series, n = 4, 5, . . . , with $\delta = 1.58$. This term defect seems reasonable since this series has a 3dσ ($3a_g$ MO) core ancestor. Wilkinson assigned the state observed at 73011 cm^{-1} (9.05 eV) as the first member of the nR′″ series. The calculated term values for the ndπ (b_{2g} MO) series are 1.52, 0.99, and 0.53 eV. The measured term value of the first member of the R′″ series is 1.47 eV. We therefore assign Wilkinson's nR‴ series as a ndπ_x series, n = 4, 5. . . , with $\delta = 1$. The first member of this series is hence a B_{1u} state

[(Σ core) (π) (b_{2g})] at 9 eV above the ground state. Note that this Rydberg state is of the same symmetry as the V state ($^1B_{1u}$) which is due to the $\pi \rightarrow \pi^*$ transition. In the united atom limit the π^* MO becomes $3d\pi_x$. Later in this section we will discuss how the relative location of the V state and this Rydberg state changes in going from the experimental to the Hartree-Fock spectrum.

We next assign transitions corresponding to the two ndδ series. These ndδ orbitals can be b_{1g} (nd_{xy}) or a_g ($nd_{x^2-y^2}$) MO's. Wilkinson's nR″ series has term values of 1.90 and 1.01 eV and a term defect of 0.32. With our present computer programs we cannot calculate the $nd_{x^2-y^2}$ series properly and our calculated term values for the nd_{xy} series are 1.51, 0.99, and 0.54 eV. We therefore assign Wilkinson's nR″ series as a $nd\delta_{cos}$, n = 3, 4, . . , series. Wilkinson tentatively assigned states at 8.92, 9.11, and 9.39 eV as members of a possible fifth nR″″ series. These give term values of 1.60, 1.41, and 1.13 eV respectively. We propose that the state at 9.11 eV is probably a vibrational member of the 4R‴ series and therefore assign the states with term values 1.60 and 1.13 eV to a nR″″ series, n = 3, 4, . . . , with a $nd\delta_{sin}$ Rydberg orbital. This accounts for the five electric dipole allowed Rydberg series possible in ethylene.

Transitions to states with configuration [Σ core) (π) (np_x, np_y, or np_z)] are electric-dipole forbidden. For example the np_y series would correspond to the electric quadrupole allowed transition $A_g \rightarrow B_{1g}$. From our calculated term values there should be B_{1g}, B_{2g},

and A_g states at 8.0 eV. The existence of these states may be a part of the explanation of the minimum in the generalized oscillator strength as a function of momentum transfer, f(K), recently observed in the electron impact spectrum of ethylene.[23] It can be shown that Rydberg and valence transitions can be distinguished by the appearance of a minimum in the curve for f(K) for Rydberg transitions while for valence transitions f(K) should decrease monotonically as K increases.[24] This argument is based on the presence or absence of radial nodes in the molecular orbitals involved in the transition. Krauss and Mielczarek[23] have used this characteristic minimum to study the Rydberg character of the excited states corresponding to energy losses of 7.16, 8.0, 8.27, and 9.12 eV. The energy losses at 7.16, 8.17, and 9.12 eV clearly correspond to Rydberg transitions $\pi \rightarrow 3s$, $\pi \rightarrow 4d\sigma$, and $\pi \rightarrow 4s$ with calculated term values 3.4, 2.3, and 1.5 eV respectively (Table X). In agreement with Miller's theoretical curves[24] minima are observed in f(K) for these three energy losses.[23] To study the orbital character of the V state they chose an energy loss of 8 eV due to the Rydberg peaks lying on top of the $N \rightarrow V$ absorption. The f(K) curve for this energy loss shows a minimum. This is surprising since the V state, with its strong oscillator strength, is usually identified with a valence transition and, like its UAO limit $2p_x \rightarrow 3d\pi$, involves orbitals with no radial nodes. One explanation is that the Rydberg contribution at an energy loss of 8.0 eV is due to dipole-forbidden Rydberg transitions that become allowed as the molecule becomes nonplanar.[23] Our calculations support

this explanation since they show three Rydberg states, $\pi \rightarrow 3p_x$, $3p_y$, and $3p_z$, at about 8 eV,[25] all of which become allowed as the molecule is distorted from the planar geometry. The energy of these Rydberg states will change very little as the CH_2 groups twist relative to each other and hence should still be at around 8 eV. The other explanation, namely that there is configurational mixing of considerable Rydberg character with the valence state is still a possibility.[23]

We predict B_{1u} Rydberg states [(sigma core)$(\pi)(nd\pi_x)$] with term values of 1.52, 0.99, and 0.53 eV. These states are of the same symmetry as the V state. Experimentally the first member should therefore be at 9 eV. However direct SCF calculations on the C_2H_4 ground state and the $C_2H_4^+$ ion give an SCF ionization potential of 9.03 eV.[4] Therefore in the Hartree-Fock approximation we can expect these B_{1u} Rydberg states to be at 7.51, 8.04, and 8.50 eV. Direct SCF calculations with a large basis flexible enough to describe both the valence (π, π^*) state and the Rydberg states $(\pi, nd\pi_x)$ give states at 7.43, 8.13, and 8.64 eV.[4,26] Surprisingly no valence-like (π, π^*) state emerges from these calculations. All the states are clearly very diffuse e.g., the state at 7.43 eV has a π^* (or $nd\pi_x$) orbital with the matrix element[27] $\langle \pi^* | x^2 | \pi^* \rangle = 42$ (a.u.)^2. It becomes obvious that only Rydberg states emerge from the SCF approximation and that in this same approximation, the valence-like state probably lies above the energy of the positive ion i.e., 9.03 eV above the ground state.[4]

B. Benzene

As a final example we shall calculate term values for various Rydberg series of benzene. The model potential of the positive ion core is again approximated by the sum of the model potentials of the six carbon atoms. For the atomic model potential we choose the parameters calibrated to the singlet Rydberg spectrum of the carbon atom (Table I) and $\delta Z = 1/6$. Based on test calculations for ethylene we neglect the contribution of the hydrogen atoms to the molecular potential. The basis set of Gaussian orbitals is shown in Table XI.

With the molecule in the x-y plane the electron configuration of the ground state ($^1A_{1g}$) in D_{6h} symmetry is

$$|A_{1g}\rangle = \{\text{core}\}\,(2e_{2g})^4(3a_{1g})^2(2b_{1u})^2(1b_{2u})^2(3e_{1u})^4(3e_{2g})^4(1a_{2u})^2(1e_{1g})^4 \tag{17}$$

with $\{\text{core}\}$ denoting the core orbitals $(1a_{1g})^2(1e_{1u})^4(1e_{2g})^4(1b_{1u})^2\,(2a_{1g})^2\,(2e_{1u})^4$. Wilkinson[28] has observed four Rydberg series in the absorption spectrum of benzene converging to the ionization potential of 9.25 eV. These series thus all correspond to excitation out of the $1e_{1g}$ orbital. The transitions of the nR and nR′ series are strong and are clearly dipole allowed. The upper states must be either $^1E_{1u}$ (xy polarized) or $^1A_{2u}$ (z-polarized) corresponding to transitions $1e_{1g} \rightarrow npa_{2u}$ and $1e_{1g} \rightarrow npe_{1u}$ respectively.[29] It has usually been assumed that the upper states of the nR series are $^1A_{2u}$ and the nR series assigned as $1e_{1g} \rightarrow npe_{1u}$. The nR′ series must then be $1e_{1g} \rightarrow npa_{2u}$ ($^1E_{1u}$ upper states). Our

calculated term values suggest the reverse assignment, namely that the nR series is $1e_{1g} \rightarrow npa_{2u}$ ($^1E_{1u}$ states) and the nR′ series $1e_{1g} \rightarrow npe_{1u}$ ($^1A_{2u}$ states). The calculated quantum defects (Table XII) are 0.49 and 0.35 for the npa_{2u} and npe_{1u} series respectively compared to Wilkinson's term defects of 0.46 and 0.16 for the observed nR and nR′ series. We therefore assign Wilkinson's nR and nR′ series to $1e_{1g} \rightarrow npa_{2u}$ and $1e_{1g} \rightarrow npe_{1u}$ transitions respectively. Note that this assignment puts a $^1E_{1u}$ Rydberg state on top of the N → V absorption. The V state is definitely $^1E_{1u}$ ($1e_{1g} \rightarrow 1e_{2u}$). We believe that these two states, although of the same symmetry, are so different that very little mixing occurs.

Wilkinson's nR″ and nR‴ series are weak and probably correspond to forbidden transitions which have gained their strength by borrowing intensity from allowed transitions. From the calculated term values (Table XII) the transitions in these series are $1e_{1g} \rightarrow nd$. We can also reasonably assign the R″ and R‴ series as $1e_{1g} \rightarrow nde_{1g}$ and nde_{2g} respectively. These series have term defects of 0.04 and 0.02.

These four series are the only Rydberg transitions studied experimentally by means of ultraviolet absorption. Lassettre[30] has studied the electron impact energy loss spectrum of benzene at high incident electron energy and small scattering angle. Under these conditions only allowed processes are observed. The excitation curve shows one very strong and broad peak at 7.0 eV, strong peaks at 9.4, 11.0, and 12.2 eV, smaller peaks at 10.4 and 13.0 eV, and a very

small peak at 12.6 eV. Jonsson and Lindholm[31] have used this spectrum ultraviolet absorption data, and the results of photoelectron spectroscopy to try to determine the orbital energy levels in ground state benzene. They assign orbital levels to the peaks in the photoelectron spectrum and, from estimated or experimental term values, deduce the resulting excitation curve which is then compared to the experimental curve. Although our assignments of certain peaks in Lassettre's spectrum disagree with theirs,[31] we predict the same orbital energy level scheme. The energies of the $1e_{1g}(\pi)$, $3e_{2g}$, and $1a_{2u}(\pi)$ orbitals are 9.3, 11.4, and 12.1 eV respectively. The $3e_{1u}$ orbital has an energy of 13.8 eV. However, from our calculated term values, we assign the peaks at 7.0 and 8.2 eV as $1e_{1g} \rightarrow 3pa_{2u}$ and $4pa_{2u}$ transitions respectively and those at 7.4 and 8.4 eV as $1e_{1g} \rightarrow 3pe_{1u}$ and $4pe_{1u}$. Our results confirm the assignment of the peak at 11.4 eV in the photoelectron spectrum as the $3e_{2g}$ level since this leads to Rydberg transitions $3e_{2g} \rightarrow 3pe_{1u}$ and $4pe_{1u}$ at 9.4 and 10.4 eV respectively in good agreement with Lassettre's peaks at 9.3 and 10.4 eV. We predict a $1a_{2u}(\pi) \rightarrow 3da_{1g}$ transition at 10.1 eV correlating very well with Lassettre's peak at 10 eV. We would also assign the $3e_{1u} \rightarrow 3sa_{1g}$ and $3e_{1u} \rightarrow 3de_{1g}$ or $3de_{2g}$ transitions, calculated at 11.3 and 12.4 eV, to the strong peaks at 11.0 and 12.2 eV respectively in the energy loss spectrum. The small unassigned peak at 12.6 eV is very probably the $3e_{1u} \rightarrow 4sa_{1g}$ predicted at 12.6 eV. Finally the peak at 12.9 eV could also be the $3e_{1u} \rightarrow 4d$ transition. The calculated term values put the $3e_{1u} \rightarrow 4d$ transition at 12.9 eV and the proposed $1b_{2u} \rightarrow 3de_{2g}$ assignment at 13.1 eV.

We anticipate that calculated term values will be very useful in the interpretation of electron impact spectra of large polyatomic molecules and consequently the assignment of orbital energies to the peaks of the corresponding photoelectron spectrum.

CONCLUSIONS

The main purpose of this work has been to develop and use simple model potentials to calculate the Rydberg series of diatomic and large polyatomic molecules. These model potentials are chosen to reproduce the main features of the exact pseudopotential, i.e., to replace orthogonality constraints in the eigenvalue equation for outer orbitals by adding a non-local potential to the single-particle Hamiltonian. To develop a practical scheme for large molecules we represented the effective potential of the molecular core by a sum of model potentials of the constituent atoms.[2] The atomic potentials are calibrated to atomic data and hence the molecular potential contains no further parameters. With Gaussian-type functions to describe the Rydberg orbital the calculations are simple and straightforward requiring little computer time.

The results are very encouraging. The calculated term values agree with the measured values to within 5-10% in all cases. The s, p, and d series emerge very distinctly not only for the diatomic

molecules but also for ethylene and benzene. For the diatomic molecules we have proposed assignments for some series, e.g., the ndσ series in N_2 and the ndπ in CO. In ethylene we have proposed quantitative assignments for all the Rydberg series observed by Wilkinson.[3] The agreement between calculated and measured term values is again 5-10%. These results have been useful in discussing the results of Hartree-Fock calculations on the excited states of ethylene. They also suggest a partial explanation of the behavior of the generalized oscillator strength as a function of momentum transfer at an energy loss of 8.0 eV in the electron impact spectrum of ethylene.[23] These applications illustrate some of the uses we anticipate for the results of these model calculations.

For benzene our calculated term values indicate that Wilkinson's nR series[28] is due to $1e_{1g} \rightarrow npa_{2u}$. The calculated quantum defect is 0.49 compared to experimental value of 0.46. This means that there is Rydberg state of the same symmetry as the V state lying on top of the $N \rightarrow V$ absorption. One can argue that there should be very little mixing of these states. We also quantitatively assign the three other Rydberg series observed by Wilkinson as $1e_{1g} \rightarrow npe_{1u}$, nde_{1g}, and nde_{2g}. A useful application of the calculated term values is in assigning orbital energies to the peaks in the photoelectron spectrum. With the photoelectron spectrum and calculated terms we can propose an excitation curve, e.g., for electron impact, which can be compared with the experimental curve.[31] In this way we have con-

firmed Jonsson and Lindholm's result that between the $1e_{1g}$ (9.3 eV) and $1a_{2u}$ (12.1 eV) π levels there is a σ ($3e_{2g}$) level at 11.4 eV.

ACKNOWLEDGMENT

We acknowledge the advice and assistance of Dr. Nicholas Winter at various stages of this work.

REFERENCES

[1]J. D. Weeks, A. Hazi, and S. A. Rice, Adv. in Chemical Phys. 16, 283 (1969).

[2]A. U. Hazi and S. A. Rice, J. Chem. Phys. 48, 495 (1968).

[3]For some experimental results in this region see P. G. Wilkinson, Can. J. Phys. 34, 643 (1956).

[4]See, for example, "The Interpretation of Open-Shell SCF Calculations on the T and V States of Ethylene," H. Basch and V. McKoy, J. Chem. Phys. September (1970).

[5]J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1969). We use the term pseudopotential in the sense of Eq. (4). We call the sum of the potential terms in H and V_s the effective potential.

[6]I. V. Abarenkov and V. Heine, Phil. Mag. 11, 529 (1965).

[7]M. Blume, W. Briggs and H. Brooks, Tech. Rep. No. 260, Cruft Lab., Havard University.

[8]R. S. Mulliken, The Threshold of Space (Pergamon Press, Inc., New York, 1957), p. 169.

[9]H. LeFebvre-Brion and C. M. Moser, J. Chem. Phy. 43, 1394 (1965).

[10]G. Herzberg, Spectra of Diatomic Molecules, (D. Van Nostrand Co., Inc., Princeton, New Jersey, 1967), p. 559.

[11]For states with the $c\,^4\Sigma_u^-$ ion core see K. Codling and R. Madlen, J. Chem. Phys. 42, 3935 (1965).

[12]J. Leclercq, Ann. de'Astrophysique, 30, 93 (1967).

[13]W. C. Price and G. Collins, Phys. Rev. 48, 714 (1935).

[14]M. Ogawa, J. Chem. Phys. 43, 2142 (1965).

[15]H. LeFebvre-Brion, C. M. Moser, and R. K. Nesbet, J. Mol. Spectry. 13, 418 (1964).

[16]S. G. Tilford, J. T. Vanderslice, and P. G. Wilkinson, Can. J. Physics 43, 450 (1965).

[17]The assignment of a ndσ series is not possible since the calculated term values are 2.38, 1.17, and 0.65 eV.

[18]K. Huber, Helv. Phys. Acta 34, 929 (1961).

[19]K. P. Huber and E. Miescher, Helv. Phys. Acta 36, 257 (1963).

[20]H. LeFebvre-Brion and C. Moser, J. Mol. Spectry. 15, 211 (1965).

[21]P. G. Wilkinson, Can J. Phys. 34, 643 (1956).

[22]See Table I and discussion in Section III.

[23]M. Krauss and S. R. Mielezarek, J. Chem. Phys. 51, 5241 (1969).

[24]K. Miller, J. Chem. Phys. 51, 5235 (1969).

[25]Direct SCF calculations involving all electrons also show these states at about 8 eV (private communication from Harold Basch).

[26]T. Dunning, W. Hunt, and W. A. Goddard, Chem. Phys. Lett. 4, 147 (1969).

[27]The x-direction is perpendicular to the plane of the molecule.

[28]P. G. Wilkinson, Can. J. Phys. 34, 596 (1956).

[29]For similar calculations on these states see A. Hazi and S. Rice, J. Chem. Phys. 48, 495 (1968).

[30]E. Lassettre, A. Skerbele, M. Dillon, and K. Ross, J. Chem. Phys. 48, 5066 (1968).

[31]B. Jonsson and E. Lindholm, Ark. Fysik 39, 65 (1969).

[32]Intensity arguments probably favor the $1e_{2u} \rightarrow 3de_{2g}$.

TABLE I. Core parameters from different atomic calibrations[a]

	Singlet[b]	Triplet
Carbon	0.375	0.205
	Doublet	Quartet
Nitrogen	0.115	0.010
	Triplet	Quintet
Oxygen	0.045	-0.035

[a]core parameters A of Eq. (5), in atomic units.

[b]these headings specify the multiplicity of the Rydberg states used in the atomic calibration.

TABLE II. Parameters for atomic model potentials.

Atom	A^a	$r_0{}^a$
C	0.375	2.5
N	0.115	2.5
O	0.045	2.5

[a] in atomic units. See Eq. (5).

TABLE III. Gaussian basis set for diatomic calculations.

	Orbital Exponents	
ns, npσ, and npπ series		
	s-functions	p-functions
Centers A[a] and B	0.45	0.45
	0.15	0.15
Molecular Midpoint	0.05	0.05
	0.0166	0.0166
	0.0055	0.0055
	0.0018	0.0018
	0.0006	0.0006
ndσ series		
Centers A[a] and B		0.45
		0.15
		0.05
Centers C[b] and D		0.0166
		0.0055
		0.0018
		0.0006
ndπ series		
Centers A[a] and B		0.15
		0.05
		0.0166
Centers C[b] and D		0.0055
		0.0018
		0.0006

[a]The atoms are at centers A and B.

[b]Center C is 3 a.u. to the right of B and center D 3 a.u. to the left of A.

TABLE IV. Rydberg levels for N_2.[a]

Rydberg orbital symmetry	Calculated term values[b]	Experimental term values	Fit to Rydberg formula[b]
$3s\sigma_g$	3.80	3.65[c]	3.77[d]
$4s\sigma_g$	1.61		1.62
$5s\sigma_g$	0.88		0.89
$6s\sigma_g$	0.53		0.57
$4p\sigma_u$	2.60	2.80[e]; 2.11[f]	2.60[g]
$5p\sigma_u$	1.23	1.26	1.26
$6p\sigma_u$	0.72	0.73	0.74
$7p\sigma_u$	0.45	0.49	0.49
$3p\pi_u$	2.63	2.21[h]	2.63[i]
$4p\pi_u$	1.26		1.27
$5p\pi_u$	0.77		0.75
$6p\pi_u$	0.47		0.49
$4d\sigma_g$	2.70	2.71[j]	2.69[k]
$5d\sigma_g$	1.35		1.29
$6d\sigma_g$	0.79		0.75
$7d\sigma_g$	0.40		0.49
$4d\pi_g$	2.52[l]		

[a]Internuclear distance of 2.113 a.u.

[b]All term values in electron volts.

[c]Average of term values for states $^1\Sigma_g^+$ and $^3\Sigma_g^+$ [$(\text{core})(2\sigma_u)^2$ -

(Table IV continued)

$(1\pi_u)^4(3\sigma_g)(ns\sigma_g)]$ at 3.4 eV and 3.71 eV respectively, o $^1\Pi_u$ [(core) $(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2(ns\sigma_g)]$ at 3.59 eV, $^1\Sigma_u^+$ [(core)$(2\sigma_u)(1\pi_u)^4(3\sigma_g)^2$ $(ns\sigma_g)]$ at 3.89 eV.

[d]With a term defect $\delta = 1.1$.

[e]Average of term values for states $p'^1\Sigma_u^+$ and $D^3\Sigma_u^+$ [(core)$(2\sigma_u)^2$ $(1\pi_u)^4(3\sigma_g)(4p\pi_u)]$ at 2.65 and 2.95 eV respectively. For experimental values listed in this column see R. S. Mulliken,"The Threshold of Space," (Pergamon Press, Inc., New York, 1957) p. 167.

[f]y $^1\Pi_g$ [(core)$(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2(4p\sigma_u)]$.

[g]With a term defect $\delta = 1.71$.

[h]Average of term values for states $^1\Pi_u$ and $^3\Pi_u$ [(core)$(2\sigma_u)^2(1\pi_u)^4$ $(3\sigma_g)(3p\pi_u)]$ at 2.11 and 2.40 eV respectively, z $^1\Delta_g$ and x $^1\Sigma_g^-$ [(core) $(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2(3p\pi_u)]$ at 2.02 and 2.29 eV respectively.

[i]With a term defect $\delta = 0.73$.

[j]h $^1\Sigma_u^+$[(core)$(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^2(4d\sigma_g)]$ at 2.71 eV.

[k]With a term defect $\delta = 1.75$.

[l]No state with this configuration has been definitely identified. See text for discussion.

TABLE V. Rydberg Levels for O_2.[a]

Rydberg orbital symmetry	Calculated term values[b]	Experimental term values[b]	Fit to Rydberg formula[b]
$3s\sigma_g$	3.97	3.71[c]	3.97[d]
$4s\sigma_g$	1.67	1.66[e]	1.67
$5s\sigma_g$	0.90	0.93[f]	0.92
$6s\sigma_g$	0.53	0.59[f]	0.58
$^g 4p\sigma_u$	2.64	2.54[h]	2.64[j]
$5p\sigma_u$	1.25	1.25[i]	1.27
$6p\sigma_u$	0.73	0.74[i]	0.75
$7p\sigma_u$	0.45	0.49[i]	0.49
$4d\pi_g$	1.55	1.49[k]	1.55[l]
$5d\pi_g$	1.02	0.83	0.87
$6d\pi_g$	0.55	0.53	0.56
$3d\sigma_g$	2.82		2.82[m]
$4d\sigma_g$	1.34		1.33
$5d\sigma_g$	0.72		0.77

[a]Internuclear distance of 2.282 a.u.

[b]All term values in electron volts.

[c]Average of term values for states $^3\Sigma_u^-$ [($^4\Sigma_u^-$ core) $3s\sigma_g$] at 3.70 eV, $^5\Pi$ and $^3\Pi$ states at 3.87 and 3.61 eV respectively arising from $^4\Pi$ of the O_2^+ ion, $^3\Pi$ and $^1\Pi$ states at 3.84 and 3.51 eV respectively arising from $^2\Pi$ of O_2^+.

(Table V continued)

[d] With a term defect $\delta = 1.15$.

[e] Average of term values for states $^3\Sigma_u^-$ [($^4\Sigma_u^-$ core) $4s\sigma_g$] at 1.70 eV; $^5\Pi$ and $^3\Pi$ states at 1.65 and 1.49 eV respectively arising from $^4\Pi$ of the O_2^+ ion, $^3\Pi$ state at 1.77 eV arising from the $^2\Pi$ of O_2^+.

[f] $^3\Sigma_u^-$ [($^4\Sigma_u^-$ core)$ns\sigma_g$] for n = 5, 6.

[g] The results for the $np\pi_u$ and $sp\sigma_u$ series are almost identical but the $np\pi$ series begins at n = 3 with $\delta = 0.74$. Experimentally the two series have not been definitely distinguished since in most cases $np\pi_u$ and $np\sigma_u$ both lead to allowed transitions.

[h] Average of term values for states arising from [($^2\Sigma_g^-$ core) $4p\sigma_u$ or $3p\pi_u$] at 2.65 eV, [($^4\Sigma_g^-$ core) $4p\sigma_u$ or $3p\pi_u$] at 2.87 eV, and [($X^2\Pi_g$ core) $4p\sigma_u$ or $3p\pi_u$] at 2.48 and 2.16 eV.

[i] Average for states arising from [($^2\Sigma_g^-$ core) $np\sigma_u$ or $np\pi_u$] and [($^4\Sigma_g^-$ core)$np\sigma_u$ or $np\pi_u$] at 1.27 and 1.22 eV respectively for n = 5, 0.74 and 0.73 eV for n = 6, 0.49 and 0.48 eV for n = 7 respectively.

[j] With a term defect $\delta = 1.74$.

[k] $^3\Pi_u$ [($^4\Sigma_u^-$ core)$nd\pi_g$] states. See reference 11 and text for discussion. We assign their state at 3.70 eV to the ns series.

[l] $\delta = 1.04$.

[m] $\delta = 0.80$.

TABLE VI. Rydberg Levels for CO[a]

Rydberg orbital symmetry	Calculated term values[b]	Experimental term values[b]	Fit to Rydberg formula[b]
$3s\sigma$	3.68	3.23[c]	3.68[f]
$4s\sigma$	1.57	1.64[d]	1.59
$5s\sigma$	0.86	0.80[e]	0.88
$6s\sigma$	0.52	0.51	0.56
$4p\sigma$	2.55	2.61[g]	2.54[i]
$5p\sigma$	1.21	1.19[h]	1.24
$6p\sigma$	0.71	0.70	0.73
$7p\sigma$	0.45	0.46	0.48
$3p\pi$	2.59	2.49[j]	2.59[l]
$4p\pi$	1.26	1.24[k]	1.26
$5p\pi$	0.73	0.73	0.74
$6p\pi$	0.46	0.48	0.49
$4d\pi$	1.58	1.73[m]	1.58[n]
$5d\pi$	1.03	0.95	0.88
$6d\pi$	0.55	0.59	0.56

[a] Internuclear distance of 2.132 a.u.

[b] All term values in electron volts.

[c] $B\,^1\Sigma^+$ state [$(X\,^2\Sigma^+$ core) $3s\sigma$]. See reference 10.

[d] Σ state [$(X\,^2\Sigma^+$ core) $4s\sigma$]. This state was previously assigned as the $F\,^2\Pi$. See text for discussion.

[e] Takamine, Tanaka , and Iwata's Rydberg series converging to the $X\,^2\Sigma^+$ core. See reference 10.

[f] With a term defect $\delta = 1.08$.

[g] $C\,^1\Sigma^+$ state [$(X\,^2\Sigma^+$ core) $4p\sigma$].

[h] The diffuse series of Tanaka's β bands. See references 10 and 14. This series converges to the $B\,^2\Sigma^+$ ion.

(Table VI continued)

[i] With a term defect $\delta = 1.72$.

[j] $^1\Pi\,[(X^2\Sigma^+ \text{ core})3p\pi]$. This state was previously assigned as $E\,^1\Sigma^+$ but correctly reassigned as a Π state in Ref. 15. See text.

[k] The sharp series of Tanaka's β bands. See Ref. 14.

[l] With a term defect $\delta = 0.74$.

[m] Our suggested assignment for Ogawa's B—X Rydberg series IV. See Ref. 14 and text for discussion and assignment of the B—X Rydberg series III.

[n] With a term defect $\delta = 1.07$.

TABLE VII. Rydberg Levels for NO[a]

Rydberg orbital symmetry	Calculated term values[b]	Experimental term values[b]	Fit to Rydberg formula[b]
3sσ	3.88	3.82[c]	3.88[g]
4sσ	1.64	1.66[d]	1.65
5sσ	0.89	0.93[e]	0.91
6sσ	0.53	0.57[f]	0.57
4pσ	2.62	2.74[h]	2.62[i]
5pσ	1.24	1.27	1.27
6pσ	0.72	0.74	0.74
7pσ	0.45	0.48	0.49
3pπ	2.65	2.78[j]	2.65[k]
4pπ	1.28	1.30	1.28
5pπ	0.74		0.75
6pπ	0.46		0.49
4dσ	2.75	2.66[l]	2.75[m]
5dσ	1.31	1.25	1.31
6dσ	0.70		0.76

[a]Internuclear distance of 2.176 a.u.

[b]All term values in electron volts.

[c]A $^2\Sigma^+$ state [($^1\Sigma^+$ core) 3sσ].

[d]Average of term values for states E $^2\Sigma^+$[($^1\Sigma^+$ core) 4sσ] and $^2\Sigma^+$ [(a $^3\Sigma^+$ core) 4sσ] at 1.72 and 1.60 eV respectively.

[e]Average of term values for states S $^2\Sigma^+$[($^1\Sigma^+$ core) 5sσ] and $^2\Sigma^+$ [(a $^3\Sigma^+$ core) 5sσ] at 0.95 and 0.90 eV respectively.

[f]Member of Tanaka's α series. See Ref. 18.

[g]With a term defect δ = 1.13.

(Table VII continued)

[h] Tanaka's β series with configuration $[(1\sigma)^2 \cdots (5\sigma)^2 (1\pi)^3 (2\pi) np\sigma]^2\Sigma^+$. These are within a few percent of the term values of the γ series.

[i] With a term defect $\delta = 1.72$.

[j] $C^2\Pi$ and $K^2\Pi$ states [($^1\Sigma^+$ core) $3p\pi$ and $4p\pi$].

[k] With a term defect $\delta = 0.74$.

[l] $D^2\Sigma^+$ and $M^2\Sigma^+$ states [($^1\Sigma^+$ core) $4d\sigma$ and $5d\sigma$]. See Ref. 19.

[m] With a term defect $\delta = 0.78$.

TABLE VIII. ns Series in Ethylene with Different Model Potentials [a]

"Singlet" C-atom potential	"Triplet" C-atom potential	H-atom model potential included
3.42	3.60	3.35
1.49	1.55	1.48
0.84	0.86	0.83

[a] All results in eV's. See section V for discussion,

TABLE IX. Gaussian Basis Set for Ethylene Calculations

	Orbital Exponents	
	p-functions	s-functions
ns and npσ series		
Molecular Midpoint	0.05	0.05
	0.0166	0.0166
	0.0055	0.0055
	0.0018	0.0018
	0.0006	0.0006
Centers A and B[a]	0.45	0.45
	0.15	0.15
ndσ series		
Centers A and B[b]	0.45	
	0.15	
	0.05	
Centers C and D[c]	0.0166	
	0.0055	
	0.0018	
	0.0006	
npπ and ndπ series		
Centers A and B[b]	0.15	
	0.05	
	0.0166	
Centers C and D[c]	0.0055	
	0.0018	
	0.0006	

[a] On the z-axis with coordinates 1.265 and -1.265 a.u. respectively.

[b] On the z-axis with coordinates 1.265 and -1.265 a.u. respectively.

[c] On the z-axis at 4.265 and -4.265 a.u. respectively.

TABLE X. Rydberg Levels for C_2H_4 [a]

Rydberg orbital symmetry		Calculated term values	Experimental term values	Fit to Rydberg formula
3s	$(4a_g)$ [b]	3.42	3.41 [c]	3.40 [d]
4s		1.49	1.62	1.51
5s		0.84	0.90	0.85
6s		0.51	0.57	0.54
4dσ	$(5a_g)$	2.32	2.26 [e]	2.32 [f]
5dσ		1.15	1.16	1.16
6dσ		0.60		0.60
4dπ	$(2b_{2g})$	1.52 [g]	1.47 [h]	1.51 [i]
5dπ		0.99		0.85
6dπ		0.53		0.53
$3p_x$	$(2b_{3u})$	2.50 [j]		2.50 [k]
$4p_x$		1.23		1.23
$5p_x$		0.74		0.73
3dδ	(a_g)		1.90 [l]	1.89 [m]
4dδ			1.01	1.01
3dδ	$(1b_{1g})$	1.51	1.60 [n]	1.50 [o]
4dδ		0.99	1.13	0.85
5dδ		0.54		0.53

[a] Carbon-carbon distance 2.53 a.u.

[b] Symmetry designation of the Rydberg orbital. The ns series is Wilkinson's nR series. See Ref. 21.

[c] Term values for the states $^1B_{3u}$ [(sigma core) π ns]. See Ref. 21.

[d] With a term defect δ = 1.

[e] Wilkinson's nR′ series. States are $^1B_{3u}$.

[f] With a term defect δ = 1.58.

[g] $^1B_{1u}$ states.

(Table X. continued)

[h] Wilkinson's nR''' series.

[i] With a term defect $\delta = 1$.

[j] A_g states [(sigma core)πnp_x]. The np_x, np_y, and np_z series have about the same term values.

[k] $\delta = 0.67$.

[l] Wilkinson's nR'' series.

[m] $\delta = 0.32$.

[n] Possibly members of Wilkinson's suggested fifth Rydberg series nR''''.

[o] $\delta \sim 0$.

TABLE XI. Basis Set for Benzene Calculations

	Orbital Exponent		Symmetry of basis function
nsa_{1g} series			
(-5.272, 0.0, 0.0)[a], $[C_6]$[b]	0.45		s
	0.15		s
(0.0, 0.0, 0.0), [E]	0.055	0.0018	s
	0.0166	0.0006	s
	0.0055	0.0002	s
npa_{2u} series			
(-6.0, 0.0, 0.0), $[C_6]$	same as ns series		z
(0.0, 0.0, 0.0), [E]	same as ns series		z
npe_{1u} series			
(-4.0, 0.0, 0.0), $[C_2]$	same as ns series		y
(0.0, 0.0, 0.0), [E]	same as ns series		y
nda_{1g} series			
(0.0, 0.0, 1.0), $[\sigma_h]$	0.45	0.05	z
	0.15		
(0.0, 0.0, 4.0), $[\sigma_h]$	0.0166	0.0018	z
	0.0055	0.0006	z
nde_{1g} series			
(-2.636, 0.0, 0.0), $[C_2]$	0.15	0.0166	z
	0.05		
(-6.0, 0.0, 0.0), $[C_2]$	0.0055	0.0006	z
	0.0018	0.0002	
nde_{2g} series			
same as nde_{1g} series			y

[a](x, y, z) coordinates locating the basis function.

[b]Symmetry operation in D_{6h} locating points with identical basis function.

TABLE XII. Rydberg Levels for Benzene[a]

Rydberg Orbital	Calculated term values	Experimental term values[b]	Fit to Rydberg Formula
$3sa_{1g}$	2.52		2.53[c]
$4sa_{1g}$	1.21		1.23
$5sa_{1g}$	0.71		0.73
$6sa_{1g}$	0.47		0.48
$3pa_{2u}$	2.16	2.32[d]	2.16[e]
$4pa_{2u}$	1.09	1.10	1.10
$5pa_{2u}$	0.66	0.66	0.67
$6pa_{2u}$	0.44	0.44	0.45
$3pe_{1u}$	2.03	1.84[f]	1.94[g]
$4pe_{1u}$	1.02	0.88	1.02
$5pe_{1u}$	0.62	0.56	0.63
$6pe_{1u}$	0.42	0.39	0.43
$3da_{1g}$	2.01		2.01[h]
$4da_{1g}$	1.01		1.02
$3de_{1g}$	1.40	1.63[i]	1.55[j]
$4de_{1g}$	0.87	0.87	0.87
$5de_{1g}$	0.60	0.56	0.56
$3de_{2g}$	1.38	1.26[k]	1.53[l]
$4de_{2g}$	0.86	0.86	0.86
$5de_{2g}$	0.58	0.55	0.55

[a] A regular hexagon with C—C distance 2.64 a.u.

[b] The electron impact spectrum shows peaks which probably correspond to nsa_{1g} and nda_{1g}. See text for these assignments.

[c] With a term defect $\delta = 0.68$.

[d] Wilkinson's nR series leading to the $^2E_{1g}$ state of $C_6H_6^+$ ion at 9.25 eV. See Ref. 28.

[e] $\delta = 0.49$.

[f] nR′ series of Ref. 28. These are $^1A_{2u}$ states.

[g] $\delta = 0.35$.

[h] $\delta = 0.40$.

[i] Wilkinson's nR″ series. This is our assignment.

[j] $\delta = 0.04$.

[k] Wilkinson's nR‴ series--our assignment.

[l] Quantum defect $\delta = 0.02$.

Appendix B

Assignments of Rydberg Series

NITROGEN ASSIGNMENTS

Band	Transition	Rydberg Orbital
$151233 - R/(n - .0701 - .0412/n)^2$ $n = 3, 4, \ldots 20$	$^1\Sigma_u^+ \leftarrow \tilde{X}$	$(ns\sigma_g)$
$151231 - R/(n + .1405 - .199/n)^2$ $n = 3, 4, \ldots 11$	$^1\Pi_u \leftarrow \tilde{X}$	$(nd\pi_g)$
$134730 - R/(n - .1906 + .075/n)^2$ $n = 3, 4, \ldots 7$	$^3\Pi_u \leftarrow \tilde{X}$	$(ns\sigma_g)$
$136598 - R/(n - .0399 - .0258/n)^2$ $n = 2, 3, \ldots 17$	$^1\Pi \leftarrow \tilde{X}$	$(ns\sigma_g)$
o′		$(3s\sigma_g)$
$125666.8 - R/(n + .3697 - .3459/n + .532/n - .960/n^4)^2$ $n = 2, 3, \ldots 31$	$^1\Sigma_u^+ \leftarrow \tilde{X}$	$(np\sigma_u)$
e		$(4p\sigma_u)$
p′		$(3p\sigma_u)$
$125666.8 - R/(n + .3142 - .0404/n - .4289/n^4)^2$ $n = 2, 3, \ldots 8$	$^1\Pi_u \leftarrow \tilde{X}$ [a]	$(np\pi_u)$
c		$(3p\pi_u)$

[a] The electronic configuration of the ground state $\tilde{X}$ $(^1\Sigma_g^+)$ of nitrogen is: $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2 - (1\pi_u)^4(3\sigma_g)^2$.

OXYGEN ASSIGNMENTS

Band	Transition	Rydberg Orbital
198125 - $R/(n - .98)^2$ $n = 3, 4, \ldots 8$	$^3\Sigma_g^- \leftarrow \tilde{X}$	$(ns\sigma_g)$ strong
198125 - $R/(n - .98)^2$ $n = 4, 5, \ldots 8$	$^5\Sigma_g^- \leftarrow \tilde{X}$?	$(ns\sigma_g)$ weak
198125 - $R/(n - .19)^2$ $n = 3, 5, \ldots 13$	$^3\Pi_u \leftarrow \tilde{X}$	$(nd\pi_g)$
163702 - $R/(n - .70)^2$ $n = 4, 6, \ldots 23$	$^3\Sigma_g^-$, $^3\Pi_u \leftarrow \tilde{X}$	$(np\sigma_u)$ or $(np\pi_u)$
163700 - $R/(n - .55)^2$ $n = 6, 8, \ldots 12$	$^3\Sigma_g^-$, $^3\Pi_u \leftarrow \tilde{X}$	$(np\sigma_u)$ or $(np\pi_u)$
146568 - $R/(n - .67)^2$ $n = 4, 6, \ldots 30$	$^3\Sigma_g^-$, $^3\Pi_u \leftarrow \tilde{X}$	$(np\sigma_u)$ or $(np\pi_u)$
146570 - $R/(n - .55)^2$ $n = 4, 6, \ldots 16$	$^3\Sigma_g^-$, $^3\Pi_u \leftarrow \tilde{X}$	$(np\sigma_u)$ or $(np\pi_u)$
15.01 eV (N)[a]	$^3\Pi_u \leftarrow \tilde{X}$	$(4s\sigma_g)$
12.95 (M)		$(3s\sigma_g)$

Band	Transition	Rydberg Orbital
14.69 (I′)	$^3\Pi_u \leftarrow \tilde{X}$	$(4s\sigma_g)$
12.58 (H′)		$(3s\sigma_g)$
14.53 (I)	$^3\Pi_u \leftarrow \tilde{X}$	$(4s\sigma_g)$
12.35 (H)		$(3s\sigma_g)$
9.91	$^3\Sigma_g^-,\ ^3\Pi_u \leftarrow \tilde{X}$	$(3p\sigma_u)$ or $(3p\pi_u)$
9.58	$^3\Sigma_g^-,\ ^3\Pi_u \leftarrow \tilde{X}$[b]	$(3p\sigma_u)$ or $(3p\pi_u)$

[a] The letter in parentheses is the spectroscopic designation of the progression.

[b] The electronic configuration of the ground state $\tilde{X}$ $(^3\Sigma_g^+)$ of oxygen is: $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2$.

NITRIC OXIDE ASSIGNMENTS

Band	Transition	Rydberg Orbital
147830 - $R/(n - .78)^2$ $n = 3, 4, \ldots 14$	$^2\Pi \leftarrow \tilde{X}$	$(np\sigma)$
135530 - $R/(n - .67)^2$ $n = 3, 4, \ldots 17$	?	$(np\sigma)$
114680 - $R/(n - 1.10)^2$ $n = 3, 4, \ldots 13$	$^2\Sigma^+ \leftarrow \tilde{X}$	$(ns\sigma)$
M	$^2\Sigma^+ \leftarrow \tilde{X}$	$(4p\sigma)$
D		$(3p\sigma)$
K	$^2\Pi \leftarrow \tilde{X}$	$(4p\pi)$
C		$(3p\pi)$
S	$^2\Sigma^+ \leftarrow \tilde{X}$ [a]	$(5s\sigma)$
E		$(4s\sigma)$
A		$(3s\sigma)$

[a] The electronic configuration of the ground state $\tilde{X}$ ($^2\Pi$) of nitric oxide is: $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(1\pi)^4(2\pi)$.

CARBON MONOXIDE ASSIGNMENTS

Band	Transition	Rydberg Orbital
$158680 - R/(n - .68)^2$ $n = 4, 5, \ldots 11$	$^1\Sigma^+, {}^1\Pi \leftarrow \tilde{X}$	$(np\sigma)$ or $(np\pi)$ sharp
$158680 - R/(n - .68)^2$ $n = 4, 5, \ldots 11$	$^1\Sigma^+, {}^1\Pi \leftarrow \tilde{X}$	$(np\sigma)$ or $(np\pi)$ diffuse
$158670 - R/(n - .96)^2$ $n = 4, 5, \ldots 9$	$^1\Sigma^+ \leftarrow \tilde{X}$	$(ns\sigma)$
$158670 - R/(n - .20)^2$ $n = 3, 4, \ldots 9$	$^1\Pi \leftarrow \tilde{X}$	$(nd\pi)$
$133380 - R/(n - .70)^2$ $n = 4, 5, \ldots 8$	$^1\Sigma^+, {}^1\Pi \leftarrow \tilde{X}$	$(np\sigma)$ or $(np\pi)$
$113029 - R/(n - .88)^2$ $n = 5, 6, \ldots 13$	$^1\Sigma^+ \leftarrow \tilde{X}$	$(ns\sigma)$
$\tilde{F}$		$(4s\sigma)$
$\tilde{B}$		$(3s\sigma)$
$\tilde{C}$	$^1\Sigma^+ \leftarrow \tilde{X}$	$(3p\sigma)$
$\tilde{E}$	$^1\Pi \leftarrow \tilde{X}$ [a]	$(3p\pi)$

[a] The electronic configuration of the ground state $\tilde{X}(\Sigma^+)$ of carbon monoxide is: $(1\sigma)^2(2\sigma)^2(3\ )^2(4\sigma)^2(1\pi)^2(5\sigma)^2$.

CARBON DIOXIDE ASSIGNMENTS

Band	Transition	Rydberg Orbital
$156410 - R/(n - .56)^2$ $n = 4, 5 \cdots, 9$	$^1\Pi_u$ or $^1\Sigma_u^+ \leftarrow \tilde{X}$	$(np\pi_u)$ or $(np\sigma_u)$
$156400 - R/(n - 1.05)^2$ [a] $\tilde{R}$ $n = 4, 5 \cdots, 8$	$^1\Sigma_g^+ \leftarrow \tilde{X}$	$(nd\sigma_g)$ $(3s\sigma_g)$?
$156350 - R/(n - .71)^2$ $n = 4, 5 \cdots, 9$	$^1\Sigma_u^+$ or $^1\Pi_u \leftarrow \tilde{X}$	$(np\sigma_u)$ or $(np\pi_u)$
$145860 - R/(n - 1.01)^2$ [b] $\tilde{R}$ $n = 4, 5 \cdots, 19$	$^1\Sigma_u^+ \leftarrow \tilde{X}$	$(ns\sigma_g)$ $(4s\sigma_g)$
$145780 - R/(n - .34)^2$ [c] $\tilde{R}$ $n = 3, 4 \cdots, 18$	$^1\Sigma_u^+ \leftarrow \tilde{X}$	$(nd\pi_g)$ $(3d\pi_g)$
$139726 - R/(n - 1.063 - .0069/n)^2$ [d] $\tilde{L}$ $n = 4, 5 \cdots, 11$	$^1\Pi_u \leftarrow \tilde{X}$	$(ns\sigma_g)$ $(4s\sigma_g)$
$139634 - R/(n - 1.044 - .34/n)^2$ [e] $\tilde{M}$ $n = 5, 6 \cdots, 10$	$^1\Pi_u \leftarrow \tilde{X}$	$(ns\sigma_g)$ $(4s\sigma_g)$

111250 - $\begin{cases} R/(n - .57)^2 \\ R/(n - .97)^2 \end{cases}$ $n = 3,4\cdots,11$ $n = 4,5\cdots,11$		$^1\Pi_g \leftarrow \tilde{X}$ $^1\Pi_g \leftarrow \tilde{X}$	$(nd\sigma_g)$ $(ns\sigma_g)$ $(4s\sigma_g)$ $(3d\sigma_g)$
111240 111060	$R/(n - .65)^2$ $n = 3,4\cdots,15$	$^1\Pi_u$ or $^1\Sigma_u^+ \leftarrow \tilde{X}^f$	$(np\sigma_u)$ or $(np\pi_u)$ $(5p\sigma_u)$ or $(5p\pi_u)$ $(4p\sigma_u)$ or $(4p\pi_u)$ $(3p\sigma_u)$ or $(3p\pi_u)$

---

[a] $156400 - R/(n - .05)^2$, Herzberg ibid., pg 597.

[b] $145800 - R/(n + .068 + 3.25/n^3)^2$, Herzberg ibid., pg 597.

[c] $145800 - R/(n - .305)^2$, Herzberg ibid., pg 597.

[d] $139726 - R/(n - .063 - .0069/n)^2$, Herzberg ibid., pg 597.

[e] $139634 - R/(n - .044 - .34/n)^2$, Herzberg ibid., pg. 597.

[f] The electronic configuration of the ground state $\tilde{X}(^1\Sigma_g^+)$ of carbon dioxide is:
$(1\sigma_u)^2(1\sigma_g)^2(2\sigma_g)^2(3\sigma_g)^2(2\sigma_u)^2(4\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^4$

NITROGEN DIOXIDE ANALYSIS

Band	Transition	Rydberg Orbital
152390, 152160 } $- R/(n - 1.03)^2$, $n = 3, 4, \ldots$	$^2\Sigma_g^+ \leftarrow \tilde{X}$	$(ns\sigma_g)$
152290 $- R/(n - .67)^2$, $n = 3, 4, \ldots, 7$	$^2\Sigma_u^+, {}^2\Pi_u \leftarrow \tilde{X}$	$(np\sigma_u)$ or $(np\pi_u)$
$\tilde{J}$		$(3p\sigma_u)$ or $(3p\pi_u)$
152100 $- R/(n - .15)^2$ [a], $n = 2, 3, \ldots, 8$	$^2\Sigma_g^+ \leftarrow \tilde{X}$	$(nd\sigma_g)$
$\tilde{I}$	$^2\Pi_u \leftarrow \tilde{X}$	$(3s\sigma_g)$?
99500 $- R/(n - .75)^2$, 97350 $- R/(n - .65)^2$, 03695 $- R/(n - .79)^2$ } ?, $n = 3, 4$	$^2\Pi_u, {}^2\Sigma_u^+ \leftarrow \tilde{X}$	$(np\sigma_u)$ or $(np\pi_u)$
$\tilde{E}$	$^2\Sigma_u^+ \leftarrow \tilde{X}$ [b]	$(3p\sigma_u)$

[a] Herzberg gives this series a quantum defect $\delta = 1.15$.

[b] The electronic configuration of the ground state $\tilde{X}(^2A_1)$ of nitrogen dioxide is: $(1b_2)^2(1a_1)^2(2a_1)^2(3a_1)^2(2b_2)^2(4a_1)^2(3b_2)^2(1b_1)^2(5a_1)^2(1a_2)^2(4b_2)^2(6a_1)$.

NITROUS OXIDE ASSIGNMENTS

Band	Transition	Rydberg Orbital
$162200 - R/(n - 1.06)^2$ [a] $n = 4, 5 \ldots, 12$	$^1\Sigma^+ \leftarrow \tilde{X}$	$(ns\sigma)$
$162200 - R/(n - .68)^2$ $n = 3, \ldots, 6$	$^1\Pi, {}^1\Sigma^+ \leftarrow \tilde{X}$	$(np\pi)$ or $(np\sigma)$
$162160 - R/(n - .58)^2$ $n = 3, \ldots, 6$	$^1\Sigma^+, \Pi \leftarrow \tilde{X}$	$(np\sigma)$ or $(np\pi)$
$162130 - R/(n - .31)^2$ $n = 3, 4, \ldots, 11$		$(nd\pi)$
$132250 - R/(n - .22)^2$ $\tilde{N}$ $n = 3, 4, \ldots, 8$	$^1\Pi \leftarrow \tilde{X}$	$(nd\pi)$ $(3d\pi)$
$132210 - R/(n - 1.0)^2$ $n = 3, 4, \ldots, 13$	$^1\Sigma^+ \leftarrow \tilde{X}$	$(ns\sigma)$

15.53 eV	$^1\Pi$, $^1\Sigma^+ \leftarrow \tilde{X}$	(5pπ) or (5pσ)
14.89		(4pπ) or (4pσ)
13.90		(3pπ) or (3pσ)
$104300 - R/(n - .68)^2$	$^1\Pi$, $^1\Sigma^+ \leftarrow \tilde{X}$	(npσ) or (npπ)
$\tilde{F}$ $n = 3,4\ldots,9$		(3pσ) or (3pπ)
$104000 - R/(n - .60)^2$	$^1\Pi$, $^1\Sigma^+ \leftarrow \tilde{X}$	(npσ) or (npπ)
$\tilde{E}$ $n = 3,4\ldots,13$		(3pσ) or (3pπ)
$104000 - R/(n - .95)^2$ [b]	$^1\Pi \leftarrow \tilde{X}$ [c]	(nsσ)
$\tilde{D}$		(3sσ)

(a) Listed as $162200 - R/(n - .06)^2$, Herzberg ibid.

(b) Not usually listed as a Rydberg series, Herzberg ibid, p. 505.

(c) The electronic configuration of the ground state $\tilde{X}(^1\Sigma^+)$ of nitrous oxide is:

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(6\sigma)^2(1\pi)^4(7\sigma)^2(2\pi)^4$$

Acetylene Assignments

Band	Transition	Rydberg Orbital
92076 - $R/(n - .50)^2$	$^1\Sigma_u^+ \leftarrow \tilde{X}$	$(nd\pi_g)$
$\tilde{D}$ $n = 3, 4 \cdots, 10$		$(3d\pi_g)$
91950 - $R/(n - .95)^2$	$^1\Pi_u \leftarrow \tilde{X}^a$	$(ns\sigma_g)$
$\tilde{C}$ $n = 3, 4 \cdots, 10$		$(3s\sigma_g)$

[a] The electronic configuration of the ground state $\tilde{X}$ ($^1\Sigma_g^+$) is:

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4$$

FORMALDEHYDE ASSIGNMENTS

Band	Transition	Rydberg Orbital
87830 - $R/(n - .40)^2$		(nd)
$\tilde{E}$ $n = 3, 4 \cdots, 8$		(3d)
87809 - $R/(n - 1.04)^2$	$^1B_2 \leftarrow \tilde{X}$	($ns a_1$)
$\tilde{F}$ $n = 3, 4 \cdots, 8$		($4s a_1$)
$\tilde{B}$		($3s a_1$)
87710 - $R/(n - .70)^2$	$^1B_2$ or $^1A_1 \leftarrow \tilde{X}$[a]	($np a_1$) or ($np b_2$)
$R/(n - .70)^2$		
$n = 3, 4 \cdots, 9$		
$\tilde{H}$		($4p b_2$)
$\tilde{D}$		($3p b_2$)
$\tilde{G}$		($4p a_1$)
$\tilde{C}$		($3p a_1$)

---

[a] The electron configuration of the ground state $\tilde{X}(^1A_1)$ is

$$(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(1b_2)^2(5a_1)^2(1b_1)^2(2b_2)^2$$

FORMIC ACID ANALYSIS

Band	Transition	Rydberg Orbital
$91370 - R/(n - .60)^2$	$^1A' \leftarrow \tilde{X}$	(npa″)
$\tilde{F}$		(4pa″)
$\tilde{C}$		(3pa″)
$\tilde{B}$	$^1A'' \leftarrow \tilde{X}^a$	(3sa′)

(a) The electronic configuration of the ground state $\tilde{X}$ ($^1A'$) is:

$(1a')^2(2a')^2(3a')^2(4a')^2(5a')^2(6a')^2(7a')^2(8a')^2(1a'')^2(9a')^2(10a')^2(2a'')^2$

DIAZOMETHANE ANALYSIS

Band	Transition	Rydberg Orbital
$72585 - R/(n - .10)^2$	$^1A_1 \leftarrow \tilde{X}$	$(nd\pi b_1)$
$\tilde{H}$		$(3d\pi b_1)$
$\tilde{I}$	$^1B_1 \leftarrow \tilde{X}^a$	$(4p\sigma a_1)$
$\tilde{F}$		$(3p\sigma a_1)$

(a) The electronic configuration of the ground state $\tilde{X}(^1A_1)$ is:

$$(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(5a_1)^2(6a_1)^2(7a_1)^2(1b_2)^2(1b_1)^2(2b_2)^2(2b_1)^2$$

KETENE ASSIGNMENTS

Band	Transition	Rydberg Orbital
77491 - R/(n - .07)	$^1A_1 \leftarrow \tilde{X}$	(ndπ)
$\tilde{H}$ n = 3, 4 · · · 8		(5dπ)
$\tilde{G}$		(4dπ)
$\tilde{E}$		(3dπ)
$\tilde{F}$	$^1B_1 \leftarrow \tilde{X}^a$	(4pσ) or (4dσ)
$\tilde{C}$		(3pσ) or (4dσ)

(a) The electronic configuration of the ground state $\tilde{X}$ ($^1A_1$) of ketene is:
$(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(5a_1)^2(6a_1)^2(7a_1)^2(1b_2)^2(1b_1)^2(2b_2)^2(2b_1)^2$

ETHYLENE ASSIGNMENTS

Band	Transition	Rydberg Orbital
9.39 eV	$^1B_{2u} \leftarrow \tilde{X}$	$b_{1g}(4d\delta)$
8.92		$b_{1g}(3d\delta)$
$\tilde{F}$	$^1B_{1u} \leftarrow \tilde{X}$	$b_{2g}(3d\pi)$
$84750 - R/(n - .4)^2$, $n = 3, 4, \ldots$	$^1B_{3u} \leftarrow \tilde{X}$	$a_g(nd\delta)$
$\tilde{D}$		$a_g(3d\delta)$
$84750 - R/(n - .6)^2$, $n = 3, 4, \ldots$	$^1B_{3u} \leftarrow \tilde{X}$	$a_g(nd\sigma)$
$\tilde{C}$		$a_g(3d\sigma)$
$84750 - R/(n - 1.09)^2$, $n = 3, 4, \ldots, 7$	$^1B_{3u} \leftarrow \tilde{X}$ [a]	$a_g(ns\sigma)$
$\tilde{E}$		$a_g(4s\sigma)$
$\tilde{B}$		$a_g(3s\sigma)$

[a] The electronic configuration of the ground state $\tilde{X}\,(^1A_g)$ of ethylene is: $(1a_g)^2(1b_{1u})^2(2a_g)^2\,(2b_{1u})^2(1b_{2u})^2(3a_g)^2(1b_{3g})^2(1b_{3u})^2$.

ALLENE ASSIGNMENTS

Band	Transition	Rydberg Orbital
82210 - $R/(n - 1.06)^2$ $\tilde{B}$ $n = 3, 4, \ldots, 8$	$^1E \leftarrow \tilde{X}$	(nsa_1) $(3sa_1)$ { two additional vibrational series observed
82210 - $R/(n - .30)^2$ $\tilde{F}$ $n = 3, 4, \ldots, 6$	$^1E, {}^1B_2 \leftarrow \tilde{X}$	$(nd\sigma a_1)$ or $(nd\pi e)$ $(3d\sigma a_1)$ or $(3d\pi e)$
82200 - $R/(n - .40)^2$ $\tilde{E}$ $n = 3, 4, \ldots, 7$	$^1E, {}^1B_2 \leftarrow \tilde{X}$	$(nd\sigma a_1)$ or $(nd\pi e)$ $(3d\sigma a_1)$ or $(3d\pi e)$
82190 - $R/(n - .55)^2$	$^1B_2 \leftarrow \tilde{X}$	$(np\pi e)$ $(3p\pi e)$
82190 - $R/(n - .70)^2$	$^1E \leftarrow \tilde{X}^a$	$(np\sigma b_2)$ $(3p\sigma b_2)$ { one additional vibrational series observed

[a] The electronic configuration of the ground state $\tilde{X}(^1A_1)$ is:
$(1a_1)^2(1b_2)^2(2a_1)^2(3a_1)^2(2b_2)^2(4a_1)^2(3b_2)^2(1e)^4(2e)^4$.

ACETALDEHYDE ANALYSIS

Band	Transition	Rydberg Orbital
$82505 - R/(n - .70)^2$	$^1A' \leftarrow \tilde{X}$	(npa″)
$\tilde{C}$		(3pa″)
$82504 - R/(n - .90)^2$	$^1A'' \leftarrow \tilde{X}^a$	(nsa′)
$\tilde{B}$		(3sa′)
$82475 - R/(n - .20)^2$		
$\tilde{E}$		

(a) The electronic configuration of the ground state $\tilde{X}(^1A')$ is something like:

$(1a')^2(2a')^2(3a')^2(4a')^2(5a')^2(6a')^2(7a')^2(8a')^2(9a')^2(10a')^2(1a'')^2(2a'')^2$

PROPYNE ANALYSIS

Band	Transition	Rydberg Orbital
91240 - R/(n - .52)^2 ?	$^1A_1 \leftarrow \tilde{X}$	(ndπe)
$\tilde{G}$		(3dπe)
91100 - R/(n - .96)^2 ?	$^1E \leftarrow \tilde{X}$	(nsσa_1)
$\tilde{C}$		(3sσa_1)
83600 - R/(n - .33)^2		
$\tilde{E}$		
83580 - R/(n - .57)^2	$^1A_1 \leftarrow \tilde{X}$	(ndπe)
$\tilde{D}$		(3dπe)
83570 - R/(n - .98)^2	$^1E \leftarrow \tilde{X}$[a]	(nsσa_1)
$\tilde{F}$		(4sσa_1)

(a) The electronic configuration of the ground state $\tilde{X}$ ($^1A_1$) is something like:

$(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(5a_1)^2(6a_1)^2(7a_1)^2(8a_1)^2(9a_1)^2(1e)^4$

ACROLEIN ASSIGNMENTS

Band	Transition	Rydberg Orbital
81516 - $R/(n - .68)^2$	$^1A' \leftarrow \tilde{X}$	(npa″)
$\tilde{D}$		(3pa″)
81500 - $R/(n - .15)^2$		(nda″)?
$\tilde{F}$		
81460 - $R/(n - .95)^2$	$^1A'' \leftarrow \tilde{X}$	(nsa′)
$\tilde{G}$		(4sa′)
$\tilde{E}$	$^1A'' \leftarrow \tilde{X}^a$	(3pa′) or (3dσa′)?

(a) The electronic configuration of the ground state $\tilde{X}(^1A')$ is something like:
$(1a')^2(2a')^2(3a')^2(4a')^2(5a')^2(6a')^2(7a')^2(8a')^2(9a')^2(10a')^2(11a')^2(12a')^2(13a')^2(1a'')(2a'')^2$

DIMETHYL ETHER ASSIGNMENTS

Band	Transition	Rydberg Orbital
$80330 - R/(n - 1.02)^2$ [a]	$^1B_2 \leftarrow \tilde{X}$	$(ns a_1)$
$\tilde{E}$		$(4s a_1)$
$\tilde{B}$ [b]		$(3s a_1)$
$\tilde{F}$	$^1B_2$ or $^1A_1 \leftarrow \tilde{X}$	$(4p a_1)$ or $(4p b_2)$
$\tilde{D}$		$(3p a_1)$ or $(3p b_2)$
$\tilde{C}$	$^1A_1 \leftarrow \tilde{X}$ [c]	$(3p b_2)$?

(a) This series is given as $80330 - R/(n - .02)^2$ by Herzberg.

(b) This member is not included in this series by Herzberg.

(c) The electronic configuration of the ground state $\tilde{X}$ ($^1A_1$) is something like:

$$(1a_1)^2(1b_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(2b_1)^2(5a_1)^2(3b_1)^2(6a_1)^2(4b_1)^2(7a_1)^2(5b_1)^2(1b_2)^2$$

1,3-BUTADIENE

Band	Transition	Rydberg Orbital
trans-butadiene		
$73115 - R/(n - .10)^2$		(nd)
$\tilde{H}$		(3d)
$73066 - R/(n - .50)^2$	$^1A_u \leftarrow \tilde{X}$	(npb_u)
$\tilde{G}$		$(4pb_u)$
$\tilde{F}$		$(3pb_u)$
$\tilde{E}$	$^1A_u \leftarrow \tilde{X}$?	$(3pb_u)$?
$\tilde{D}$	$^1B_u \leftarrow \tilde{X}$ [a]	$(3pa_u)$
cis-butadiene		
$70606 - R/(n - .10)^2$	$^1A_1 \leftarrow \tilde{X}$?	(nda_2)?
$\tilde{C}$	$^1B_1 \leftarrow \tilde{X}$	$(3pb_2)$
$\tilde{B}$	$^1B_2 \leftarrow \tilde{X}$ [b]	$(3pb_1)$

(a) The electronic configuration of the ground state $\tilde{X}$ (^1A_g) of trans-butadiene is:
$(1a_g)^2(1b_u)^2(2b_u)^2(2a_g)^2(3a_g)^2(3b_u)^2(4a_g)^2(4b_u)^2(5a_g)^2(5b_u)^2(6a_g)^2(6b_u)^2(7a_g)^2(1a_u)^2(1b_g)^2$

(b) The electronic configuration of the ground state $\tilde{X}(^1A_1)$ of cis-butadiene is:
$(1a_1)^2(1b_2)^2(2b_2)^2(2a_1)^2(3a_1)^2(3b_2)^2(4a_1)^2(4b_2)^2(5a_1)^2(6a_1)^2(5b_2)^2(6b_2)^2(7a_1)^2(1b_1)^2(1a_2)^2$

2-BUTENE ANALYSIS

Band	Transition	Rydberg Orbital
trans-butene		
$74000 - R/(n - .24)^2$	$^1A_u \leftarrow \tilde{X}$	$(nd\sigma)$
$73900 - R/(n - .88)^2$	$^1A_u \leftarrow \tilde{X}^a$	(ns)
cis-butene		
$73550 - R/(n - 1.03)^2$	$^1B_1 \leftarrow \tilde{X}^b$	(ns)

(a) The electronic configuration of the ground state $\tilde{X}(^1A_g)$ of trans-butene is:

$$(1a_g)^2(1b_u)^2(2a_g)^2(2b_u)^2(3a_g)^2(4a_g)^2(3b_u)^2(5a_g)^2(4b_u)^2$$
$$\times \quad (6a_g)^2(5b_u)^2(7a_g)^2(6b_u)^2(8a_g)^2(7b_u)^2(1a_u)^2$$

(b) The electronic contribution of the ground state $\tilde{X}(^1A_1)$ of cis-butene is:

$$(1a_1)^2(1b_2)^2(2a_1)^2(2b_2)^2(3a_1)^2(4a_1)^2(3b_2)^2(5a_1)^2(4b_2)^2(6a_1)^2(5b_2)^2$$
$$\times \ (7a_1)^2(6b_2)^2(8a_1)^2(7b_2)^2(1b_1)^2$$

BENZENE ASSIGNMENTS

Band	Transition	Rydberg Orbital
13.1 eV	$^1E_{1u} \leftarrow \tilde{X}$	$(3de_{2g}) \leftarrow (1b_{2u})$[a]
12.9 eV	$^1E_{1u} \leftarrow \tilde{X}$	$(4de_{1g})$ or $(4de_{2g}) \leftarrow (3e_{1u})$
12.2 eV		$(3de_{1g})$ or $(3de_{2g}) \leftarrow (3e_{1u})$
12.6 eV	$^1E_{1u} \leftarrow \tilde{X}$	$(4sa_{1g}) \leftarrow (3e_{1u})$
11.0 eV		$(3sa_{1g}) \leftarrow (3e_{1u})$
10.0 eV	$^1A_{2u} \leftarrow \tilde{X}$	$(3da_{1g}) \leftarrow (1a_{2u})$
10.4 eV	$^1E_{1u} \leftarrow \tilde{X}$	$(4pe_{1u}) \leftarrow (3e_{2g})$
9.3 eV		$(3pe_{1u}) \leftarrow (3e_{2g})$
$74587 - R/(n - .04)^2$, n = 3.4	$^1B_{1g}? \leftarrow \tilde{X}$	(nde_{2g})
$\tilde{K}$		(nde_{2g})
$\tilde{G}$		$(3de_{2g})$
$74587 - R/(n - .11)^2$, n = 3.4	$^1A_{1g}? \leftarrow \tilde{X}$	(nde_{1g})
$\tilde{J}$		$(4de_{1g})$
$\tilde{F}$		$(3de_{1g})$

BENZENE ASSIGNMENTS (Continued)

Band	Transition	Rydberg Orbital
$74587 - R/(n - .16)^2$, n = 3, 4	$^1A_{2u} \leftarrow \tilde{X}$	(npe_{1u})
$\tilde{I}$		$(4pe_{1u})$
$\tilde{E}$		$(3pe_{1u})$
$74587 - R/(n - .46)^2$, n = 3, 4	$^1E_{1u} \leftarrow \tilde{X}^b$	(npa_{2u})
$\tilde{H}$		$(4pa_{2u})$
$\tilde{D}$		$(3pa_{2u})$

(a) The initial orbital of the electron, which is $(1e_{1g})$ unless otherwise specified.

(b) The electronic configuration of the ground state $\tilde{X}$ $(^1A_{1g})$ of benzene is:

$$(1a_{1g})^2(1e_{1u})^4(1e_{2g})^4(1b_{1u})^2(2a_{1g})^2(2e_{1u})^4(2e_{2g})^4(3a_{1g})^2(2b_{1u})^2(1b_{2u})^2(3e_{1u})^4(1a_{2u})^2(3e_{2g})^4(1e_{1g})^4$$